

USE OF BINDERS FOR PRESSING NON-PLASTIC MATERIALS

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ABSTRACT

The supply of pre-formed materials (granules, flakes, etc.) for porcelain tile manufacture can produce logistical problems relating to wear or abrasion during transport, as well as important variations in moisture content, especially when delivery is over long distances.

This study addressed the feasibility of using binders that allow producing pre-formed materials from non-clayey compositions free of moisture. In a first stage, binders of different families were tested, to subsequently study the influence of certain polyvinyl alcohol characteristics, such as molecular weight and degree of substitution, on granule properties and behaviour.

It is shown that the use of this type of binder allows producing spray-dried powder, granules and flakes, without clay or moisture, with good pressing behaviour and sufficient wear resistance to permit handling. This facilitates marketing these materials without problems associated with changes of moisture content and generation of dust.

Problems relating to binder combustion have not been observed, enabling use of these materials "in mass". The advantages of this decorating technique are greater simplicity in pressing, on not needing special facilities, and high press productivity.

The binding properties that PVA contributes open up possibilities for using materials with very different characteristic to current ones, to broaden the range of aesthetic effects in porcelain tile, such as glassy materials and glass-ceramics, metals, metal alloys, colouring metal oxides, etc.

1. INTRODUCTION

The appearance of porcelain tile in the 70s meant the incorporation of a new ceramic product into the range of existing ceramic tiles. The high technical performance of the product (high mechanical strength and frost resistance, resistance to chemical agents and abrasion, etc.) has allowed extending ceramic tile applications, opening up market areas where other materials were traditionally used (urban furnishing, high traffic areas, industrial flooring, facade cladding, etc.)^[1].

Porcelain tile, a product initially characterised by its excellent technical properties, has in recent years acquired high aesthetic qualities thanks to the development of new materials: granules, soluble colorants, flakes, micronised materials, etc., as well as the implementation of different decorating techniques: screen printing, double charges, in-press powder decoration, masks, etc.

The progressive incorporation of pre-formed powder materials, granules and flakes, to produce certain aesthetic effects, such as transparency, metallic reflections, intense colours, etc., has led to the creation of departments or specific sections in the frit, glaze and ceramic pigment manufacturing companies, dedicated to the production and supply of these materials to porcelain tile manufacturers.

The supply of pre-formed materials can generate certain logistical problems relating to wear or abrasion during transport, as well as to important variations in moisture content, especially when these materials travel large distances. In the first case, an important quantity of dust is produced that needs to be eliminated to avoid unwanted effects in the pieces, while in the second case, material properties can be altered, which considerably influences behaviour during tile pressing (low deformability, poor integration in the piece, etc.)^[2].

A solution to these problems is having pre-formed moisture-free material, with high wear resistance and appropriate behaviour in tile pressing.

Although the use of clayey compositions without any moisture allows producing wear resistant granules, it leads to inadequate behaviour during pressing. This is because moisture content acts as a plasticiser for the clay, favouring deformation and plastic flow during pressing. It therefore does not appear very appropriate to use moisture-free clayey compositions to produce these materials.

The elimination of clay in these compositions, whose main function is that of a binder, necessarily implies the addition of certain additives that take over this function. Otherwise there will be difficulties in forming compacts (granules and flakes) from these compositions, with sufficient mechanical strength and wear resistance to enable appropriate transport and handling.

In this work the feasibility was studied of using alternative binders to the clay-water system, traditionally used in ceramic tile manufacture, which allow producing pre-formed materials with adequate wear resistance (generating hardly any dust), as well as appropriate behaviour in the different porcelain tile production process stages (pressing, burnout, etc.).

2. EXPERIMENTAL

2.1 MATERIALS

To carry out the study a composition was used, consisting of a mixture of sodium feldspar, quartz and talc, whose characteristic are detailed in Table 1. These raw materials are commonly used in ceramic tile manufacture ^[3]. Different types of binders and plasticisers were also used, which will be described in the course of the paper.

SiO ₂ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	CaO (%)	MgO (%)	Na ₂ O (%)	K ₂ O (%)	ppc (%)	S _{esp} (m ² /g)	d ₅₀ (μm)
80.9	9.07	0.09	0.64	3.12	5.00	0.20	0.90	0.55	9.5

S_{esp} : Specific surface; d₅₀: Mean volume diameter

Table 1. Characteristics of the composition used.

2.2 EXPERIMENTAL PROCEDURE

The work consisted of producing pre-formed materials using the composition indicated in Table 1 together with the different binders involved in the study. Granulation was chosen out of the different existing methods for pre-forming the composition, for which a Loedige laboratory granulator was used ^[4].

The procedure used for granulation consisted of spraying the binder to be studied, after dissolving it in water, on the ceramic composition being stirred inside the granulator. The required binder concentration was calculated beforehand for the targeted aqueous solution, so that the preset binder content was obtained on granulating the composition.

These granules were then dried in an oven at 110°C, so that drying would occur in the most uniform possible way. Finally a size fraction was obtained in the range 1-5 mm by dry sieving, which was used for the characterisation tests.

The tests carried out to evaluate the suitability of a given binder were as follows:

- Wear resistance.
- Compaction diagram. Yield pressure and maximum bulk density
- Axial expansion.
- Visual evaluation of granule deformability.

The procedures used for conducting the tests mentioned are briefly described below.

Wear resistance

The wear resistance of the granules was evaluated determining the dust generation that takes place when these are stirred, to simulate the transport and handling processes.

In this way the effectiveness of the binder was evaluated in producing granules with appropriate strength to allow handling.

For this purpose a certain quantity of granules was introduced in a milling jar, and placed in a planetary mill for 60 seconds. The granules were then dry sieved at 200 μm mesh. The undersize, expressed as a percentage, represents the dust produced, which is inversely proportional to the wear resistance of the granules.

Compaction diagram

The compaction diagram provides information on the behaviour of the granules during pressing. It consists of determining the evolution of bulk density with pressure in a given pressing cycle. According to different studies ^[5,6,7], the decrease in porosity and pore size during the compaction process takes place by the following three mechanisms:

- I. Reordering of the granules to improve packing density.
- II. Reduction of the intergranular void volume by plastic deformation and/or granule break up.
- III. Decrease of intragranular porosity (the porosity of the granule) by particle slippage and reordering, producing a more densely packed arrangement.

Figure 1 shows an idealised granulated powder compaction diagram. The first slope change occurs at a pressure known as yield pressure (P_f), which is a measure of granule mechanical strength, because after this, granule break up/or deformation (mechanism II) commences.

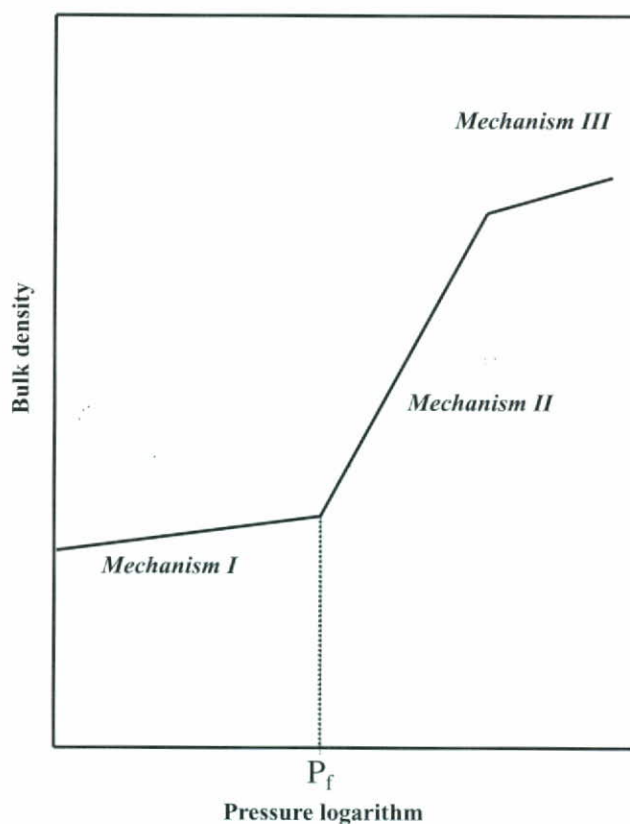


Figure 1. Compaction diagram of a granulated powder.

To determine these diagrams test specimens were formed by uniaxial pressing in a universal testing machine using a stainless steel die of 4 cm diameter, with a constant displacement speed of 5 mm/min, until reaching a maximum pressure of 400 kg/cm². This machine allows registering pairs of applied load-frame position values, which enable calculating the pressure applied at each moment and specimen bulk density.

To avoid the influence of non-uniform die filling in the compaction diagrams, after introducing the granules, the system is tapped so that the granules adopt the densest possible packing and, therefore, high reproducibility. The tests were carried out at least three times with a view to obtaining more accurate results.

Axial expansion

Axial expansion or increase of specimen thickness after concluding the compression stage is a measure of the material's elastic reaction ^[8].

Axial expansion is calculated from the following equation:

$$EP = \frac{e_d - e_c}{e_c} \cdot 100$$

where: EP: axial expansion (%)
 e_d : specimen thickness after springback
 e_c : specimen thickness at 400 kg/cm²

EVisual evaluation of granule deformability

The degree of granule integration in the spray-dried powder matrix, depends fundamentally on the deformation that the granules undergo during pressing. To assess this aspect, the surface was observed of test specimens formed at 400 kg/cm² with a stereoscopic microscope fitted with a camera. This enabled observing the presence of cracks and heterogeneities, such as granule boundaries, which indicate the degree of deformation that the granules underwent.

3. SELECTION OF THE BINDER FAMILY

In the literature surveyed numerous materials are mentioned that have a bonding effect, which are classified in terms of their colloidal or molecular nature, as well as of their organic or inorganic character ^[9].

In this first part of the work organic binders of a molecular type were used, which have been added in a percentage of 1.0%, with the exception of Xanthane Gum, whose proportion, owing to the high viscosity that it contributes to the aqueous solution, was reduced to 0.1%. Table 2 presents the binders used in this stage of the work, together with their technical characteristics.

Family	Polysaccharides	Acrylic resins	Polymerised alcohols	Cellulose ethers	Natural gums
Type	--	Ammonium polyacrylate	Polyvinyl alcohol	Carboxymethyl cellulose	Xanthane Gum
Molecular weight	Medium	Medium	Medium	Low	$2 \cdot 10^6$
Degree of substitution	--	--	88*	0.8	--
Reference	PS	ACR	PVA	CMC	GX

* Degree of hydrolysis

Table 2. Characteristic of the binders used.

One of the most important characteristics that granules should present is high wear resistance, to avoid generating dust as far as possible during transport and handling prior to tile pressing. This ensures appropriate flowability of the granulate [10] and the absence of aesthetic defects in the pieces, such as the so-called "bands". Similarly, it is also important for the granules to behave suitably in pressing, i.e., to exhibit appropriate deformability at working pressures. Unfortunately on numerous occasions, both properties are opposites, due to their dependence on granule mechanical properties, so that a balance is required.

The results obtained in granule characterisation are detailed in Table 3. The table shows the results found with a spray-dried powder usually employed to manufacture porcelain tile (PA).

The table shows that PVA and CMC are the binders that provide the granules with the greatest wear resistance, followed by ACR and PS. Finally there are the granules made with GX, in which dust generation is very high, probably due to the low added quantity (0.1%). If these values are compared with those corresponding to the spray-dried powder (PA), it is observed that all the tested binders provide notably lower wear resistance, as a result of the excellent bonding properties that clayey minerals contribute to the ceramic compositions. This fact indicates that the binder proportion to be used should exceed 1%, to reduce the quantity of arising dust.

Reference	ACR	PVA	PS	CMC	GX	PA
Moisture content (%)	<0.3	<0.3	<0.3	<0.3	<0.3	5.0
Compactness (g/cm ³)	1.76	1.76	1.80	1.77	1.74	1.89
Yield pressure (kg/cm ²)	0.6	3.5	1.5	6.0	0.5	3.0
Dust generated (%)	58	19	54	30	100	1.5

Table 3. Characteristics of the granules made.

The observed tendency agrees, in general lines, with the yield pressure values calculated from the compaction diagrams. Thus, the binders that increase granule wear resistance also provide higher yield pressure values, because, as already mentioned, both characteristics are related to granule mechanical properties.

Finally, though the compactness of all the test specimens at high pressures (400 kg/cm²) is similar, the use of strong binders such as PVA and CMC can impede total deformation of the granules. This would lead to producing pieces with large-size defects (pores and cracks) owing to the poor integration of the granules in the spray-dried powder matrix. In fact the images in Figure 2 show that the pieces made of granules with high yield pressure (PVA and CMC) exhibit very defined granule borders and large-size pores whose triangular form indicates that they come from the union of three granules (intergranular pores). In contrast, the surface of the other pieces (PS, ACR and GX) presents no heterogeneities, indicating that the granules have been completely deformed. This confirms the relationship between yield pressure and granule degree of deformation, and shows the problem associated with the use of poorly deformable granules.

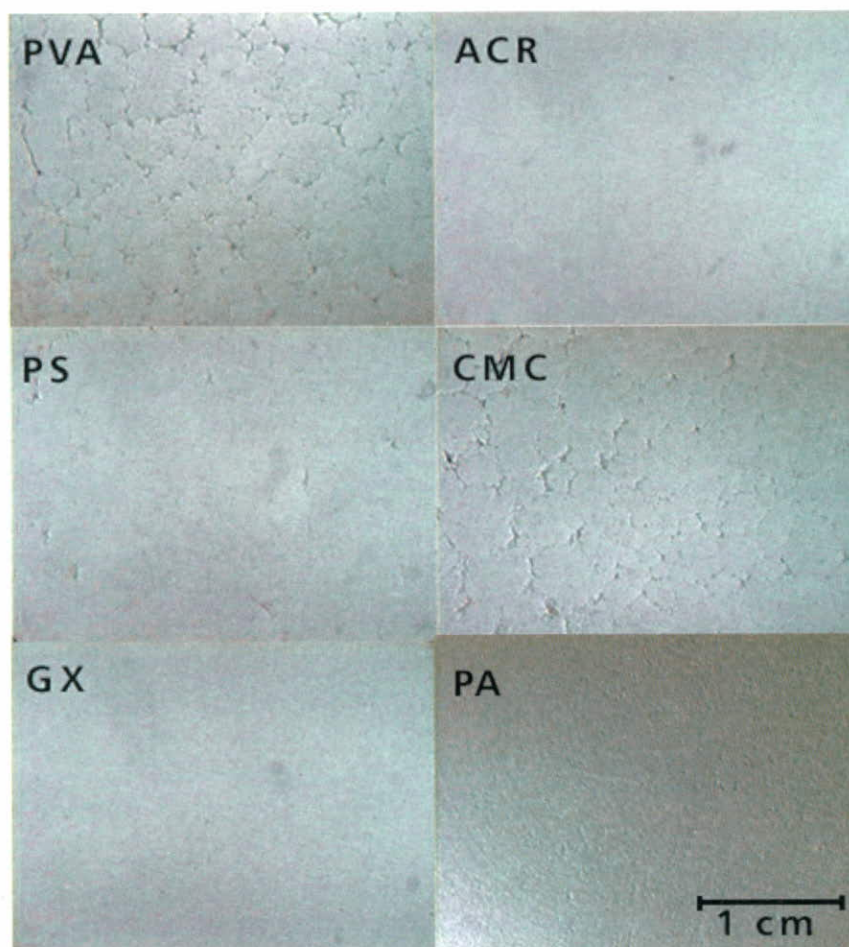


Figure 2. Surface appearance of the pieces made with granulate produced with different binders.

Based on these results, polyvinyl alcohol was chosen as the most appropriate binder family to continue the study. The acrylic resins and polysaccharides were discarded owing to the poor bonding power of the additives used in the test proportions, although binders of these families may exist with better properties. Xanthane gum was also discarded because of the difficulty of obtaining low viscosity aqueous solutions. Finally, the reasons for not selecting carboxymethylcellulose were its higher combustion temperature and the smaller wear resistance that it contributes to the granules compared with PVA, despite providing the largest yield pressure.

4. INFLUENCE OF PVA CHARACTERISTICS

Polyvinyl alcohol properties mainly depend on their degree of polymerisation (DP), which is directly related to their molecular weight and degree of hydrolysis (DH). In terms of degree of polymerisation, the classification is based on the viscosity that 4% PVA aqueous solutions provide at 20 °C. The main groups are the low viscosity one, with values around 5 cP, the medium viscosity group between 20 and 30 cP, and the high viscosity group between 40 and 60 cP. These three groups correspond to degrees of polymerisation of 500, approximately 1700 and 3500. As regards the degree of hydrolysis, two main groups exist, that of fully hydrolysed PVA (DH>98%) and that of partly hydrolysed PVA (DH=87-89%) [11].

To study the influence of the characteristics of polyvinyl alcohol on the properties of the granules, 6 types of PVA were chosen with different degrees of hydrolysis and polymerisation. Table 4 sets out the characteristics of the tested PVA, together with the properties they contribute to the granules. In this part, the added PVA percentage was 2%, with a view to reducing the tendency to generate dust to levels similar to those of spray-dried powder.

Reference	B-88	M-88	A-88	B-98	M-98	A-98
Degree of polymerisation	630	1400	4200	600	1400	4300
Degree of hydrolysis	88	88	88	98	98	98
Moisture content (%)	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
Compactness (g/cm ³)	1.69	1.66	1.64	1.69	1.67	1.62
Yield pressure (kg/cm ²)	4.0	5.0	10	5.5	6.5	12
Dust generated (%)	5.9	4.8	5.0	4.4	4.1	3.2

Table 4. Characteristics of the PVA used and resulting granules.

In the first place, it can be observed that the increase in binder proportion M-88 (used in the previous section) considerably raises granule wear resistance, going from dust generation values of 19% to 4.8% on using 1% and 2% PVA respectively.

The granule abrasion resistance found with all the tested PVA, though less than that of the spray-dried powder, is considered appropriate, since this material is subjected to less intense handling. The table shows a slight increase in abrasion resistance as the degree of polymerisation and hydrolysis of the PVA used rises.

Figure 3 plots yield pressure versus PVA degree of polymerisation. It can be observed that the values plotted are grouped as a function of the degree of hydrolysis of the PVA used, the fully hydrolysed PVA producing granules with a higher yield pressure. Moreover, at both degrees of hydrolysis, granules with a higher yield pressure are produced as the degree of polymerisation increases, this effect being more pronounced than that of the degree of hydrolysis.

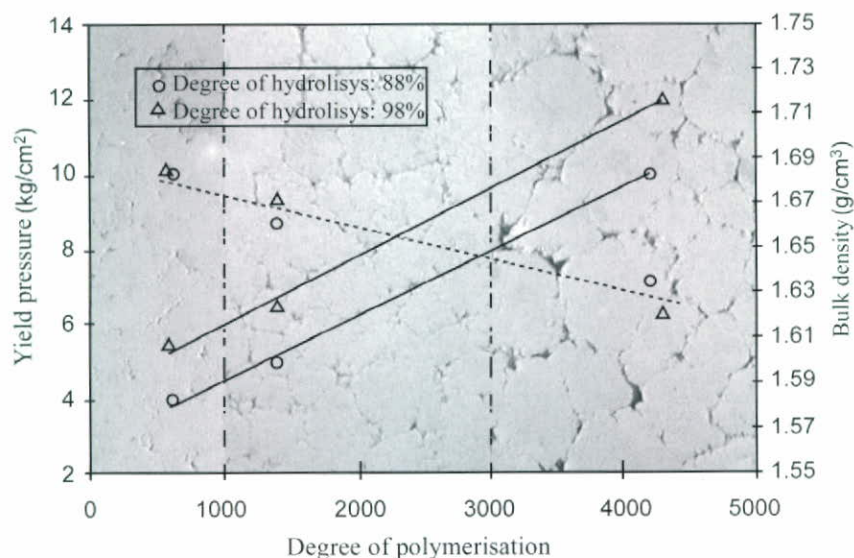


Figure 3. Evolution of yield pressure (—) and bulk density (-----) in terms of PVA characteristics.

At the bottom of the figure, the variation in the appearance of the tiles pressed with granules of different yield pressure can be observed. Only those of the partly hydrolysed PVA series are depicted. They show that as the degree of polymerisation increases, and with it granule yield pressure, their contours become clearer, indicating that scarce deformation has occurred during pressing.

Both characteristics (wear resistance and yield pressure) are related to the mechanical properties that PVA contributes to the granules, so that the observed tendencies will be related to the variation of PVA mechanical properties when the degree of hydrolysis and polymerisation alter.

The bonding properties of PVA are due to the high capacity of these polymer chains to link up as a result of hydrogen bridge formation. Figure 4a schematically illustrates the structure of a fully hydrolysed PVA, representing their carbon skeleton as a broken line, with the hydroxyl groups (OH) linked to alternate carbons. When two chains get close enough, they can align in such a way that the hydrogen in one of the hydroxyl groups can interact with the oxygen of the hydroxyl group belonging to the adjacent chain. Although the strength of this bond is relatively weak compared to that of a covalent bond, the numerous hydrogen bridges that form in the chains yield a strong bond [12,13].

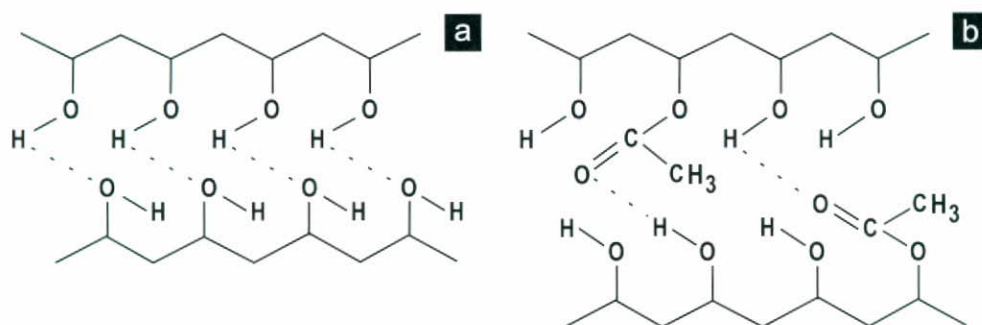


Figure 4. Schematic representation of PVA: a) fully hydrolysed PVA and b) partly hydrolysed PVA.

On the other hand, PVA has a great affinity for adhering to particles with oxygen in their basal planes, such as clay, quartz, talc and feldspar particles. In this type of materials, the hydrogens of the PVA hydroxyl groups form hydrogen bridges with the oxygen atoms present in the SiO_2 tetrahedron layers, causing the PVA molecules to be strongly adsorbed on the particle surfaces. ^[14]

The films obtained with fully hydrolysed PVA are known to provide better mechanical properties than those produced with partly hydrolysed PVA ^[15]. This is due to the presence of acetyl groups (COO-CH_3) in the partly hydrolysed PVA acting as "spacers", preventing the PVA chains from excessively approaching each other and orienting themselves appropriately (Figure 4b). Although hydrogen bridging continues between adjacent chains, the greater bond length reduces bond strength, and with fewer links, leads to poorer mechanical properties. On the other hand, the mechanical strength of PVA films increases with the degree of polymerisation, due to the larger number of C-C links, with high bond strength, as chain length increases. ^[14]

Figure 3 plots the bulk density values of the test specimens pressed at 400 kg/cm^2 . It shows that as the PVA degree of polymerisation increases, less compact test specimens are produced. This fact is related to the mechanical properties of the granules whose influence on behaviour during pressing can be clearly noted in the compaction diagrams shown in Figure 5.

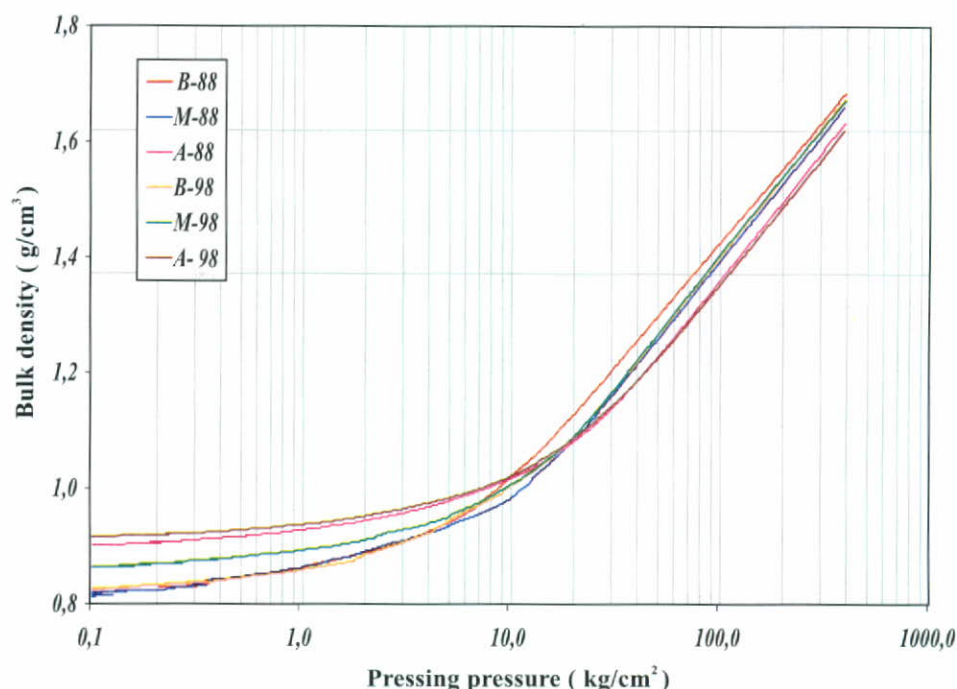


Figure 5. Compaction diagrams of granules with different PVA.

In these diagrams two clearly differentiated areas are observed, corresponding to the first two steps of the compaction process.

The first step takes place at very low pressures (less than 10 kg/cm²), with slight granule rearrangement, which leads to a very minor rise in compactness, only slightly above die filling density. The second step begins when granules begin to deform at the contact points, after exceeding yield pressure. The progressive deformation of the granules on increasing pressing pressure reduces porosity and intergranular pore size in the piece, which leads to an appreciable rise in compactness. At higher pressures, the third compaction step takes place, in which the large pores between the granules as well as their contours have already disappeared. In this step the compaction process is due to particle rearrangement forming denser packings. The third step is characterised by a drop in the compaction diagram slope, an aspect not observed in this work at the tested pressures (below 400 kg/cm²).

As mentioned, when the PVA degree of polymerisation and hydrolysis increases, the resulting granules possess better mechanical properties, making them more resistant to deformation. This implies that the second compaction step begins at higher pressures, which delays the densification process and provides the pieces with lower compactness values. This effect is clearly observed in Figure 5, in which the diagrams shown can be classified in three groups. The first corresponds to PVA B-88, with the lowest yield pressure, the second to PVA M-88, B-98 and M-98, with intermediate values, and the third group to PVA A-88 and A-98 with the greatest yield pressure. Thus, as granule yield pressure increases, the second stretch of the diagram is observed to progressively shift toward the high pressure area, which leads to the production of more porous pieces.

The use of 2% PVA reduces dust generation in all the cases to appropriate values, so that the selection of the most suitable PVA for granulation will depend on other factors, such as pressing behaviour, ease of binder handling and combustion temperature. It has been demonstrated that PVA of low molecular weight provide the best behaviour during pressing (lower yield pressure and greater compactness). These PVA are more soluble, producing solutions with lower viscosity, while also decomposing at lower temperatures. In contrast, the PVA with a high degree of polymerisation harden the granules excessively, hindering their integration with the matrix, while they decompose at higher temperatures and need to be dissolved with heat ^[11,16]. For these reasons, PVA B-88 was selected to continue the work, due to the lower yield pressure that it provides the granules with, compared with B-98.

5. INFLUENCE OF PVA CONTENT

In this section the effect of PVA B-88 content on granule properties was studied. For this, granules were prepared with PVA contents between 0 and 4%, which were used in the different characterisation tests.

Figure 6 plots the variation of dust generation on modifying PVA content. The first binder additions, up to 2%, notably increase granule wear resistance, while higher contents only produce a slight improvement of this characteristic. This indicates that the PVA content to be used should in no case be less than 2.0%, otherwise dust generation can be very high.

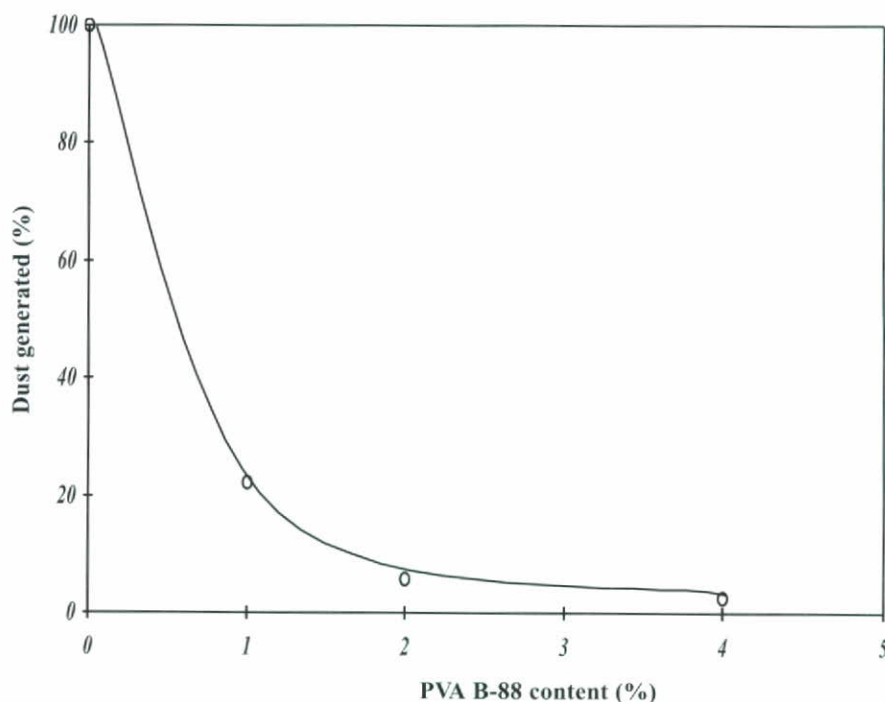


Figure 6. Evolution of dust generation with PVA B/88 content.

The compaction diagrams of the different granulates are shown in Figure 7. There is a noticeable difference between the pressing behaviour of the granules without and those with the binder. In fact, the diagram corresponding to the granules without binder exhibits a fast rise in compactness at low pressures, as a result of the weak mechanical properties of the granules (yield pressure is very low, practically zero). However, the granules with PVA exhibit a certain resistance to deformation, which delays commencement of the second step of the compaction process. This effect becomes more pronounced as binder proportion increases, leading to the production of pieces with lower dry bulk density values across the whole range of tested pressures.

Figure 8 depicts the evolution of granule yield pressure with the PVA content. The dependence of granule yield pressure (P_f) on the characteristics of the binder and of the granule can be described according to the following equation ^[17]:

$$P_f = K \cdot \left(\frac{1-p}{p} \right) \cdot \frac{V_L}{V_s} \cdot F_L$$

Where:

p : granule porosity

V_L : binder volume

V_s : solid volume

F_L : binder mechanical strength in the fracture plane

K : constant

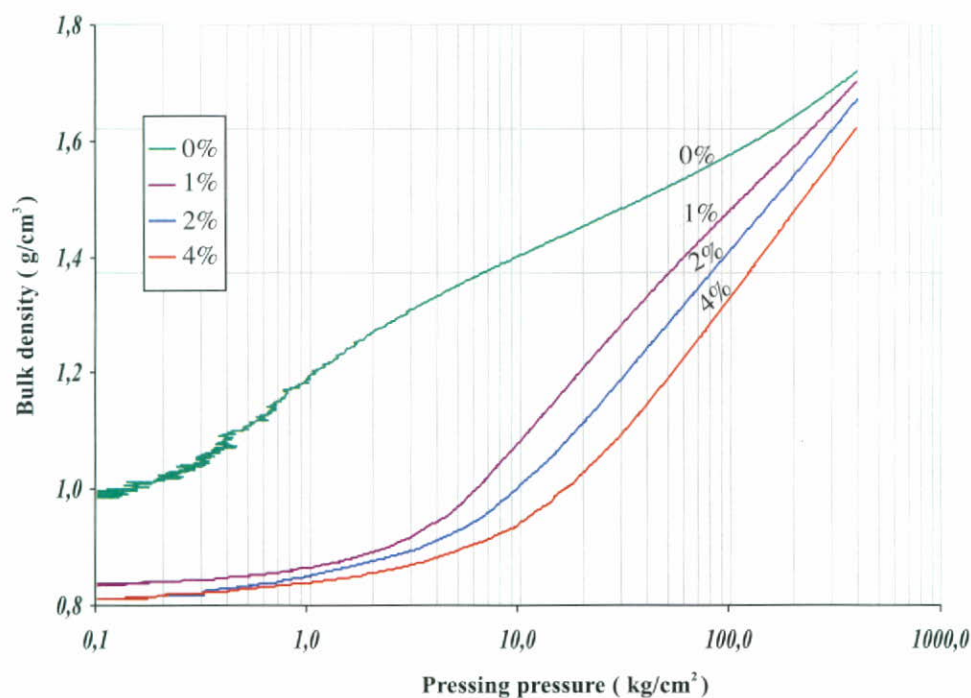


Figure 7. Compaction diagram for different PVA contents.

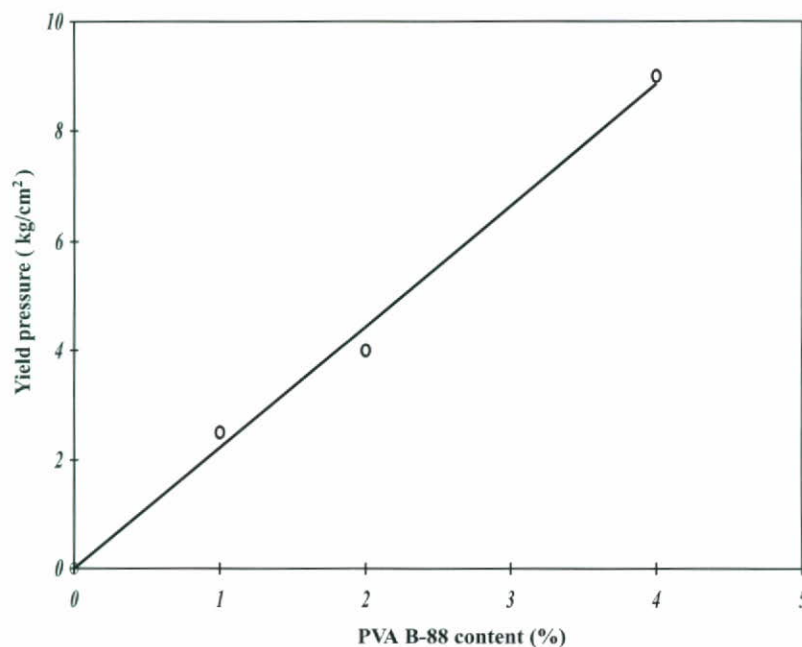


Figure 8. Variation of yield pressure with PVA B-88 content.

On raising the PVA proportion in the granules, binder mechanical strength (F_L) as well as granule porosity can be assumed not to vary significantly. In contrast, the relation V_L/V_s increases linearly with binder proportion. Indeed, Figure 8 shows that the variation of yield pressure with binder content fits a straight line, which validates the previous equation and explains the increase in yield pressure that occurs with PVA content.

To establish the type of relation that exists between granule mechanical strength and specimen compactness, Figure 9 plots specimen bulk density versus granule yield pressure found with different percentages of PVA. It is observed that as yield pressure increases, bulk density decreases, the relation being of a linear type in the range of studied values. The figure also shows the axial expansion of the pieces, and it can be observed that this decreases progressively with rising yield pressure. It indicates that on raising the binder proportion, the elastic response of the pieces decreases, as a result of greater granule rigidity. Indeed, the presence of binders such as PVA enhances the mechanical properties of the pieces, including Young's modulus. This effect produces a smaller elastic deformation of the granules during pressing, causing a reduced elastic response after the compression stage.

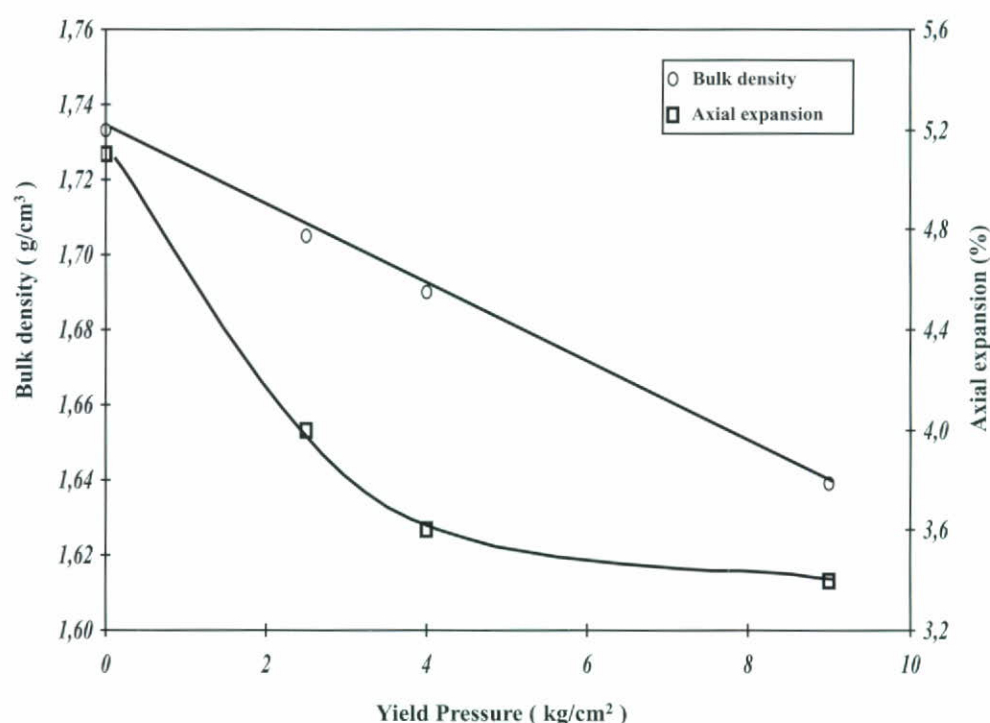


Figure 9. Variation of bulk density and axial expansion as a function of yield pressure.

Finally, with a view to visualising the degree of granule deformation, Figure 10 shows the surfaces of the test specimens pressed with different PVA percentages. The relation between yield pressure and granulate deformability is again evident, since as the proportion of PVA increases the degree of granules deformation decreases noticeably.

To sum up this section, it can be stated that the PVA content should not be below 2.0% because of the high dust generation that would take place during granule transport and handling. On the other hand, on raising the PVA content of the granules, they behave less appropriately during the pressing stage, which obliges establishing a compromise between both properties. The results obtained in this work indicate that the PVA content which balances both properties is located around 2.0-2.5%.

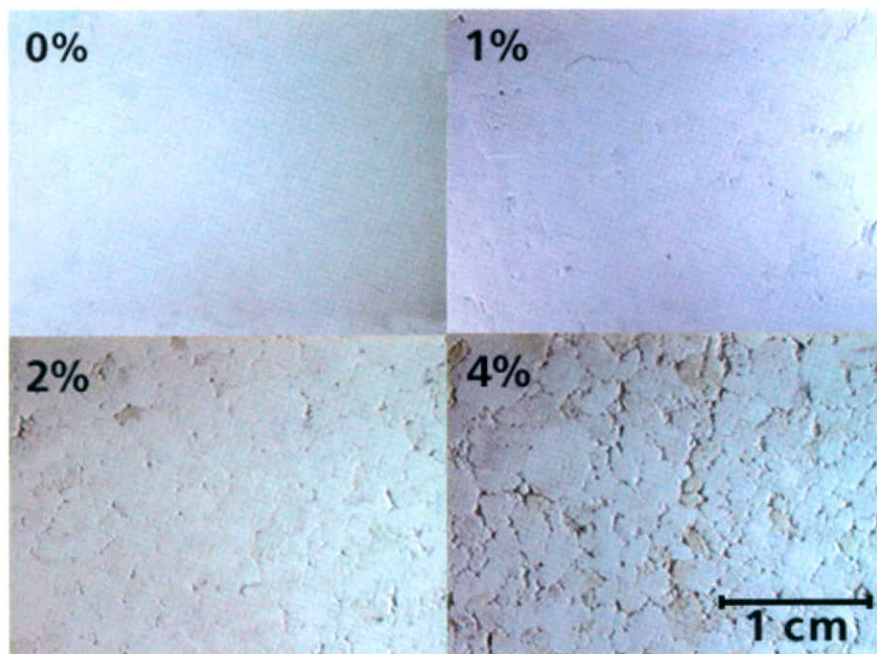


Figure 10. Surface appearance of the pieces formed on modifying the PVA B-88 quantity.

6.CONCLUSIONS

The following conclusions can be drawn from the study:

- The production of pre-formed powder materials without clay necessarily requires using another type of binder to produce granules or flakes with appropriate mechanical properties. These granules should exhibit sufficient deformability during pressing to be integrated in the piece without generating an excessive quantity of dust during handling.
- Of the different binders studied in this work, only the families of polymerised alcohols and cellulose esters provided bonding properties. This does not imply that binders may not exist in other families, different from those tested, with suitable properties.
- The yield pressure calculated from the compaction diagrams is a parameter that appropriately quantifies granule mechanical strength and, therefore, granule deformability during pressing.
- It has been shown that the mechanical properties of the granules made with PVA improve as the degree of polymerisation and hydrolysis rises. This is due to the type and quantity of the links that form between the PVA chains.
- The problem associated with the use of granules having excessive mechanical strength has been demonstrated. Although these granules have high wear resistance, their deformability during pressing is poor, which hinders integration in the piece and generates large-size cracks. It is therefore necessary to find a compromise between both properties.

- The PVA that most appropriately balance the granule characteristics are the partly hydrolysed ones of low molecular weight. This type of PVA provides appropriate wear resistance and sufficient deformability in pressing. They are also simpler to dissolve, producing less viscous suspensions and decompose fully at lower temperatures compared to fully hydrolysed PVA of high molecular weight.
- It has been shown that the proportion of PVA B-88 to be used is located around 2%. Smaller quantities notably reduce wear resistance, while higher contents excessively harden the granules hindering their behaviour during pressing.

7. INDUSTRIAL APPLICATION

The industrial applications from the study are as follows:

- The use of this type of binders enables producing spray-dried powder, granules and flakes free of moisture, with good pressing behaviour and sufficient wear resistance to allow handling. This facilitates marketing these materials without the problems associated with changes in moisture content and dust generation.
- The small binder additions together with the decrease in combustion temperature, facilitate the tile outgassing stage during preheating, enabling use of these materials "in mass". The advantages of this decorating technique are the greater simplicity during pressing, on eliminating the need for special facilities, and high press productivity.
- The bonding properties that PVA contributes open up the possibility of using materials with very different characteristics to current ones, to enable broadening the range of aesthetic effects in porcelain tile. Some of the materials that have been tested, together with their resulting effects follow:
 - glassy and glass-ceramic materials: transparency (depth), intense colorations, high whiteness.
 - metals and alloys: metallic reflections of different types
 - colouring metallic oxides: intense colorations and natural effects

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