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Processing a detergent powder formulation: Direct compression, and high shear wet granulation followed by compression

Marie-Elise Chateau, Laurence Galet*, Yannick Soudais, Jacques Fages

Laboratoire de Génie des Procédés des Solides Divisés UMR CNRS 2392, Ecole des Mines d'Albi-Carmaux, 81013 Albi-France

Abstract

In this paper, detergent tablets processing for industrial multi purpose uses, i.e., hard surfaces cleaning, has been investigated. The detergent formulation is a complex blend of over 95% of powders: inorganic salts of alkaline metal called builders, and a system of surfactants composed of anionic and nonionic organic molecules. Two processes were examined: wet granulation prior to compression (processing 1), and direct compression (processing 2). Wet granulation is performed in a laboratory high shear mixer with a blend of powdered raw materials excluding one of the salts, the metasilicate. This blend is called "initial blend for granulation." The granulation parameters studied are the intensity of shear related to the impeller speed, and the amount of liquid added, water being used as liquid binder. Powdered and granulated formulations are characterized in terms of particle size distribution, flowability, and compressibility. Compression is performed on a uniaxial laboratory press, either with the granules mixed with sodium pentahydrated metasilicate for processing 1, or with a mix of powdered and pre granulated raw materials, called here "initial blend for direct compression," for processing 2. The following features of the compacts are considered: mechanical strength, friability, density, solubility in cold water, and microscope observation of fractured surfaces. Comparison of compacts showed that prior granulation leads to increased mechanical properties due to higher plasticity and stronger binding with water, while it slightly deactivates the alkaline product. Compression of the material significantly increases dissolution times in both cases.

Keywords: Formulation; Detergent; Wet granulation; Compression

1. Introduction

Literature is poor in solid detergent manufacture for hard surface cleaning. This is mainly due to the fact that formulae based on high amounts of liquid active com pounds are usually chosen for their good efficiency on such substrates. Detergents in tablet form present the following advantages: they are more reliable to use, easier to dose, and safer for the consumer since there is no spillage or dust. From an environmental point of view, tablets reduce volumes for transport and storage, which leads to reduced packaging and use of less chemicals. They were introduced in 1998 in Europe, and quickly reached then exceeded 50% of the laundry detergents market share in countries like France or Germany. They are either manufactured using continuous rolling compaction, or uniaxial compression process. The powder is compressed directly, or undergoes a preliminary stage of granulation. Spray drying was the most prevalent granulation process until the emergence of high density powders in the end of the 1980s. NTR processes for "non tower route processes" represent from this time on new available agglomeration techniques for detergents. Compared to spray drying, the installation is small in volume and allows high energy savings [1 3].

Granulation is the process of agglomerating particles together into larger aggregates. The advantages of agglom

erated particles compared to the initial powder are better flowability, reduction of dust, ability to bind together raw materials, which might separate by segregation during transport and storage. High shear wet granulation is a size enlargement process by addition of a liquid binder onto the particles as they are stirred in a high shear mixer. Bad wet granulation results in caking, segregation, and poor compressibility. Non viscous binders with high surface tension form liquid bridges between the particles, which is the necessary condition for the formation of solid bridges. In the 1970s, Sastry and Fuerstenau developed an approach to the size enlargement mechanisms occurring in the mixer during wet granulation. The first step is wetting and nucleation, followed by two concurrent phenomena: agglomeration (coalescence, coating and abrasion transfer), and size reduction (scattering, breakage and attrition) [4]. More recently, based on the same mechanisms, Iveson et al. defined in 2001 the notion of "induction growth" at low deformation rate of the granule, and the notion of "steady growth" at high deformation rate [5].

The aim of this work is to compare the properties of compacts obtained by direct compression with the properties of compacts obtained by compression of the detergent powder, previously granulated. For this, a first study on granulation involving two parameters was carried out in a laboratory high shear mixer. Three mixing regimes (bumping flow at low shear, roping flow at high shear, and an intermediate regime), and two liquid/solid ratios using water spray as binder addition, were tested. What is the most convenient granulation processing run with the considered formulation and device, knowing that a particle size distribution centered on 0.8 1 mm is to be reached? The second part of this work deals with the comparison of the two compacted materials, powder and granules, based on the mechanical properties of the compact (friability and diameter rupture resistance), density and binding forces. Finally, the influence of both processes on solubility in cold water of the detergent material was investigated.

2. Materials and methods

2.1. Raw materials

Formulations are complex mixtures of raw materials that impart different properties to the final solid dosage product. The raw materials of the detergent formulation have been selected according to both cleaning efficiency on hard surfaces [6] and technical ability to be processed in a solid state. The formulation considered is mainly composed of over 70% w/w sodium inorganic salts, called builders, and between 10% and 20% of surfactants. The chosen builder system is based on sodium tripolyphosphate, sodium carbonate, and sodium pentahydrated metasilicate. The first two inorganic salts, phosphate and carbonate, are available from suppliers both in powdered and pre granulated forms. The powdered forms are used here for the "initial blend for granulation," processing 1, while the pre granulated forms are used for the "initial blend for direct compression," processing 2. Nonionic surfactants are organic liquids with high degreasing efficiency, which are necessary to insure good wetting of the substrate by the detergent solution. Therefore, it has been decided to adsorb nonionic surfactants previously on sodium carbonate, the most represented salt in the builder system. Sodium pentahydrated metasilicate is a water sensitive pre granulated raw material. This therefore is not used during the wet granulation step and is added to the rest of the formulation right just before compression.

2.1.1. In the case of processing 1 (granulation prior to compression)

The "initial blend for granulation" is a mix of impregnated powdered sodium carbonate with other fine dry powders, homogenized in the mixer bowl before granulation. The resulted granules are dried, then sieved with a 1.6 mm sieve, and manually mixed with the corresponding amount of sodium pentahydrated metasilicate before compression.

2.1.2. In the case of processing 2 (direct compression)

The "initial blend for direct compression" is a mix of impregnated pre granulated sodium carbonate with other powdered and pre granulated raw materials, manually blended just before compression.

2.2. Powder formulation and granules: processing and characterization

2.2.1. High shear mixer and mixer torque rheometer

Granulation is carried out in a high shear mixer (Diosna®), starting with 1500 g of "initial blend for granulation" in a 6 l bowl. Temperature of the bowl was controlled by continuous circulation of water at 20 °C in the jacket. The liquid binder (water at 20 °C) is sprayed in very small droplets using a peristaltic pump, and a bifluidic nozzle with constant air pressure of 0.6 bars, with a flow rate of 200 g/min. Nucleation occurs when a liquid drop penetrates the powder bed due to capillary force and mechanical dispersion and forms a nucleus granule [7]. The water bottle placed on a balance is used to follow and control the binder addition. The chopper speed is fixed at 1500 rpm. Binder addition rate, impeller speed and liquid/solid ratio are three independent factors, which have to be set. Power consumption of the impeller motor, widely used for end point determination and scale up, is followed on the computer screen, as well as temperature in the bowl.

A mixer torque rheometer (Caleva®) is an apparatus for measuring rheological properties in granulation and is

extensively used for binder feed end point determination. Starting with 40 g of "initial blend for granulation" on which the liquid binder is progressively sprayed, the curve of the torque value (in N m) versus the liquid/solid ratio (in ml/g) is related to the successive states in the wet mass. The maximum torque value corresponds to the capillary state, where all the pores are filled up with the binder [8].

2.2.2. Fluidized bed, and infra red balance

The wet mass obtained in the mixer bowl after granulation is dried in a fluidized bed, at 60 °C. Air flow is regulated to give a constant fluidization regime. The water content of the resulting granules is measured with an infrared balance. The moisture content is expressed as percent of water evaporated in a test carried out on 3 g of granules during 90 min at 115 °C.

2.2.3. Flowability and compressibility

The Carr index (IC, in percent), the Hausner ratio (RH), and the angle of repose are related to two rheological features of powders: flowability and compressibility. The first two parameters are deduced from aerated and tapped densities of the powder bed, as follows:

$$\mathrm{IC} = \frac{d_{\mathrm{tapped}} - d_{\mathrm{aerated}}}{d_{\mathrm{tapped}}} \times 100 \quad (1)$$

$$\mathrm{RH} = \frac{d_{\mathrm{tapped}}}{d_{\mathrm{aerated}}} \quad (2)$$

where d_{aerated} is the aerated density, and d_{tapped} is the tapped density (g/cm^3). Free flowing powders have low IC (<18%), and low HR (<1.25), and a small angle of repose (<25°). In contrast, cohesive, high compressive powders have high IC (>20%), high HR (>1.4) and large angles of repose. The densities and angles of repose are measured using a Hosokawa PT N® powder tester. In this apparatus, the angle is measured from the cone formed by the powder falling by gravity with a vibrating system.

2.2.4. Particle size distribution

Particle size distributions of raw materials and blends are determined using a laser diffraction particle size analyzer Malvern Mastersizer 2000® with the dry dispersion unit. Particle size distribution of the granules is measured by dry sieving with sieves according to the French Afnor norm NF X 11 501. The span of the curve, related to the broadness of the distribution, is determined by:

$$\mathrm{span} = \frac{d_{90} - d_{10}}{d_{50}} \quad (3)$$

where d_x is the particle diameter, for which x (w/w%) of the particles has a diameter smaller than this value.

2.3. Tabletting and properties of compacts

2.3.1. Uniaxial press

Uniaxial compression powder processing is performed on an Instron® press. The maximum compression force is 30 kN, and the compression cycle of strain (in MPa) against displacement of the upper punch (in cm) is registered. The compacts obtained with the matrix have a diameter of 30 mm, a density (d) and a thickness (e) depending on the formulation and the amount of material. For direct compressions, 15 g of the "initial blend for direct compression" is mixed before being introduced in the compression chamber. The applied compression pressure is 20 kN.

2.3.2. Mechanical properties: diametric rupture resistance and friability

F is the force (in N) required to break down the compact across its diameter. It is measured with the an Erweka

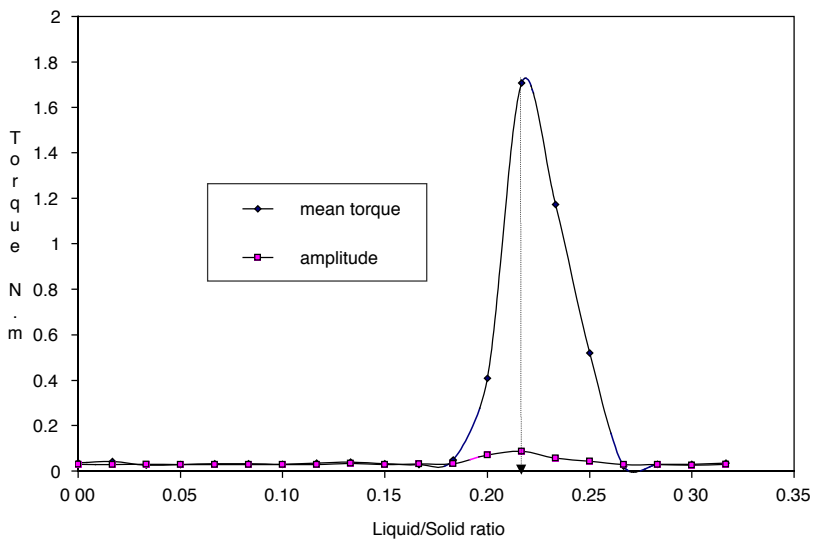

Fig. 1. Torque versus liquid/solid ratio, for the selected powdered formulation and water.

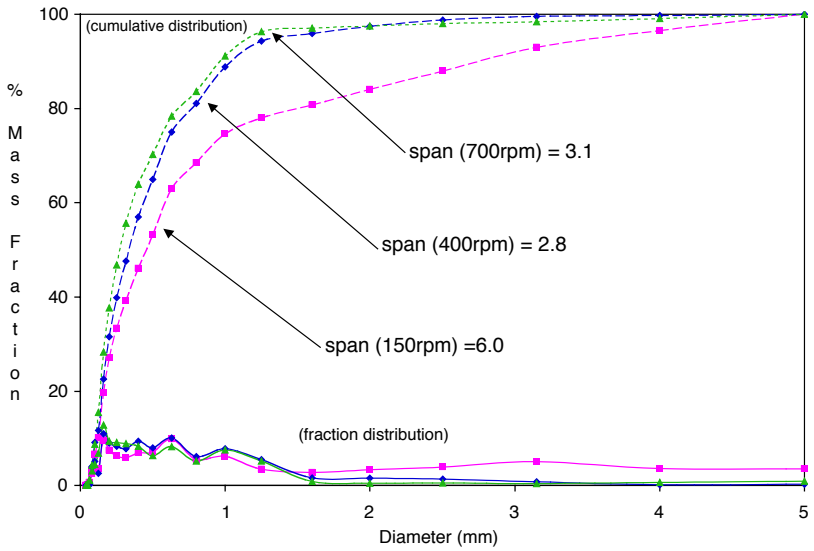

Fig. 2. Particle size distribution with a liquid/solid ratio of 0.10.

TBH30 apparatus, and the maximum diametrical stress R_D (in MPa) is deduced as follows:

$$R_D = \frac{2F}{\pi De}.10^{\ 6} \tag{4}$$

where D and e are, respectively, the compact diameter and the thickness (in m). Friability is measured with an Erweka TAR 20 apparatus. The compact is put inside a plastic wheel equipped with a baffle, which turns at constant speed for a pre determined time. The compact falls under gravity from a height of 15 cm at each rotation. The friability test protocol consists in determining the w/w% of particles obtained smaller than 5 mm after 60 rotations at 20 rpm.

2.4. Solubility in cold water

Dissolution speeds in water with controlled hardness at 25 °C are determined by conductivity measurements (in mS/cm), according to the following procedure: the product to be tested is first introduced in a 2 l beaker containing 1 l of water. 5 min later, gentle agitation of the aqueous solution is started by rotation of a dispersion impeller at 200 rpm. Conductivity values are recorded every 10 s, from the introduction of the detergent in water until the

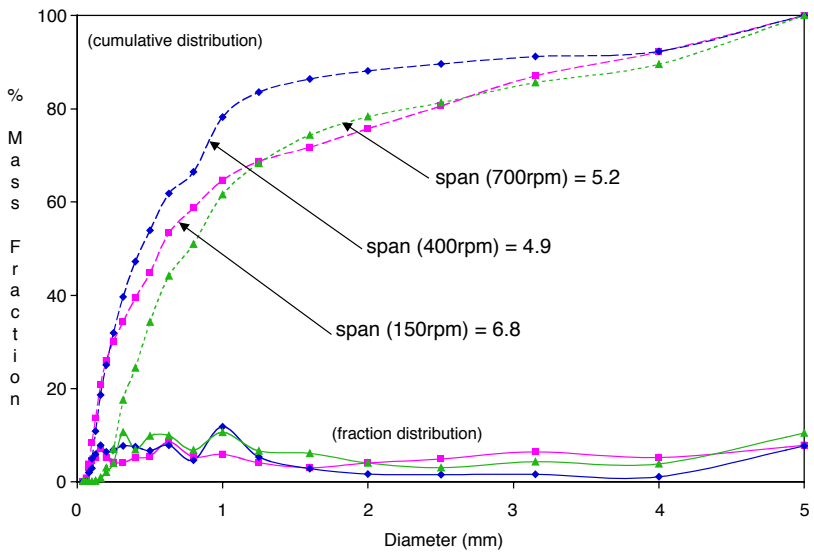

Fig. 3. Particle size distribution with a liquid/solid ratio of 0.15.

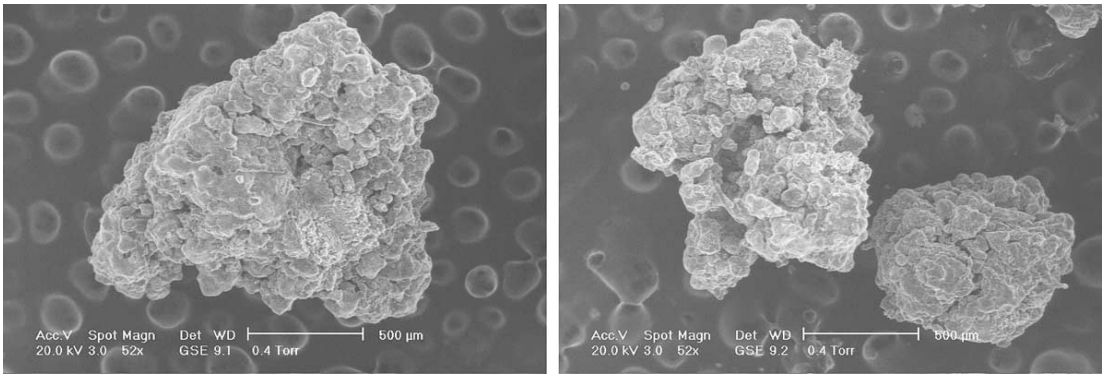

Fig. 4. SEM pictures of granules (Formulation A, impeller speed of 500 rpm).

complete dissolution of the inorganic salts. A maximal conductivity value is then reached, characterized by a plateau.

3. Results and discussion

3.1. Determination of the granulation parameters

A preliminary study was performed in the mixer torque rheometer, to set the studied limits of the liquid/solid ratio. Thereafter, trials were carried out in the high shear mixer granulator.

3.1.1. Torque rheometer results

Tap water is chosen as liquid binder (surface tension of 72.8 mN/m) and is progressively added to 40 g of "initial blend for granulation." The curve of the torque versus the ratio liquid/solid is shown in Fig. 1.

The capillary state is reached for a liquid/solid ratio of 0.22. The signal amplitude is low, which means that the mixture of powder and liquid remains homogeneous during structuration. For high shear granulation trials, it is essential not to reach the capillary state, and to end the granulation before complete saturation is reached. Therefore, the chosen limits for the liquid/solid ratio are 0.10 and 0.15.

3.1.2. Study of shear and liquid/solid ratios

The shear regime is related to the impeller speed and has been chosen at 150 rpm for bumping flow, 700 rpm for roping flow, and 400 rpm for the intermediate regime. The size distribution curves for each regime are shown in Fig. 2 with a liquid/solid ratio of 0.10, and on Fig. 3 with a ratio of 0.15.

For a ratio of 0.10, increasing speed from 150 rpm to 400 rpm avoids the formation of large agglomerates: 20% of granules larger than 1.60 mm are formed at 150 rpm, instead of less than 5% at 400 rpm. Even higher shear (700 rpm) gives similar granule size distribution results as at 400 rpm. The span value is close to 3, while it is equal to 6 at 150 rpm. For a liquid/solid ratio of 0.15, increased speed (400 rpm instead of 150 rpm) avoids the formation of large 2 4 mm granules: the amount is reduced by one third and one half. Higher shear (700 rpm) provides larger particles again: the amount of particles larger than 1.6 mm is twice the amount obtained at 400 rpm. The intermediate regime (400 rpm) corresponds again to the lower span value (4.9) and gives granules with the narrowest size distribution. An increase of the liquid/solid ratio from 0.10 to 0.15 leads to broader particle size distribution. For an impeller speed of 400 rpm, where the change is the most relevant, the span value is increased to 80%, from 2.8 to 4.9.

Particle size distributions at 400 rpm are narrower than at 150 rpm, whatever the liquid/solid ratio. Indeed, higher shear leads to a more homogeneous distribution of the liquid binder on the moving powder, favoring wetting and nucleation steps, which are essential in the granulation process. The higher the liquid/solid ratio, the closer the processing conditions to the saturation (capillary state). According to the preliminary study on the mixer torque rheometer, a ratio of 0.10 corresponds to 45% of saturation, while a ratio of 0.15 corresponds to 68% of saturation. In the first case, the main granulation mechanism is nucleation, while in the second case, the saturation rate is high enough

Table 1
Rheological values measured on dry powder and granules

Parameters	Water content (%)	d_{50} (µm)	Span	Angle of repose	Carr index [IC (%)]	Hausner ratio [HR]
Initial blend for granulation	1.8	103 ± 1	4.80 ± 0.03	49	31	1.46
Resulted granules	8.6	606 ± 6	1.84 ± 0.01	36	13	1.15
Initial blend for direct compression					21	1.27

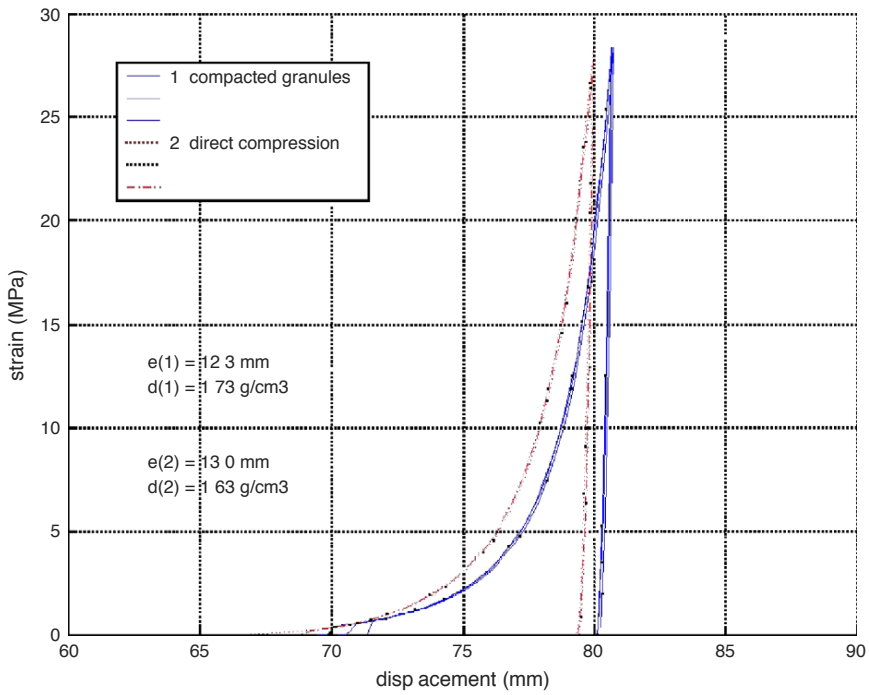

Fig. 5. Compression cycles of dry powder and granules with "*d*" and "*e*," respectively, the compact density and thickness.

to allow rapid growth regimes, such as coalescence or coating of large particles by fine particles. SEM observa tions of granules on Fig. 4 shows grape shaped clusters, which indicate that coalescence is the prominent growing regime.

3.2. Comparison of initial blend for granulation, resulting granules, and initial blend for direct compression

The chosen granulation parameters were an impeller speed of 500 rpm, and a liquid/solid ratio of 0.15. Compacts were made as follows: 15 g of material was mixed manually and introduced in the compression chamber of the press. The maximum applied force was 20 kN, and the compres sion cycle was recorded.

3.2.1. Rheological properties of the blends

Results are shown in Table 1. Granulation leads to materials with lower Carr index IC and Hausner ratio HR: IC = 31% and HR = 1.46 for with the "initial blend for granulation" characteristic of very cohesive and compres sible powders, which reduces down to IC = 13% and HR = 1.15 for the final granules. This is characteristic of poor compressible free flowing spherical particles. As expected, the poor flowing initial blend of powders acquires very good flow. Decrease of the angle of repose confirms the improvement of flow, and SEM observations on Fig. 4 show that granules are almost spherical. In comparison, the "initial blend for direct compression" has intermediate compressible, flowing and cohesive properties: IC = 21 and HR = 1.27.

3.2.2. Mechanical properties of the compacts

Compression cycles of both products (the prepared granules mixed with metasilicate, and the "initial blend for direct compression") are shown in Fig. 5. The maximum punch displacement on the *x* axis is 93 mm. Compact densities and mechanical properties (friability and diametric rupture resistance) are compared in Table 2. Environmental SEM observations of fracture surfaces are shown in Fig. 6.

The "initial blend for direct compression" contains 1.8% of water, while the granules contain 8.6% of water. Both compression cycles have a similar shape: a concave compression phase, characterizing poor compression ability, and a straight punch return phase, characterizing low volume expansion after molding. The diametrical rupture resistance is three times higher for the compact made after granulation: 0.498 MPa compared to 0.157 MPa. Finally, the compact obtained by direct compression is friable (3%), while the compact made after granulation is not friable. SEM observations of the transversal rupture surface show that in the case of compaction after granulation, raw materials are more tightly bound together than in the other

Table 2
Properties of compacts made by direct compression and compression of granules

	Compacted granules	Direct compression
Compact density (g/cm^3)	1.61	1.51
Diametric rupture resistance (MPa)	0.50	0.16
Friability (w/w%)	0	3

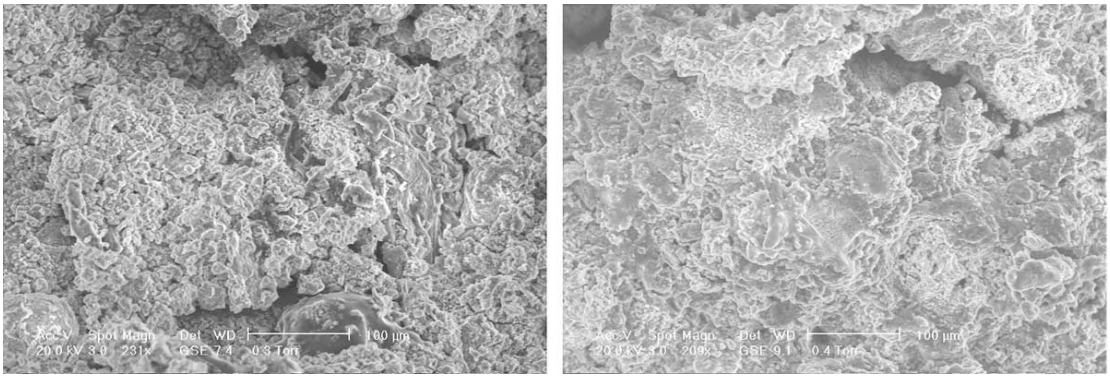

Fig. 6. SEM pictures of the compacts breaking surfaces.

case. Higher water content leads to high cohesion and plastic deformation, which defines the stress resistance of the material, its ability to be compressed without rupture or degradation [9]. The prevalent phenomena for direct compression are fragmentation and granular rearrangement. Cohesion forces are an explanation for higher mechanical properties (high rupture resistance and no friability) in the case of a compact obtained after a previous granulation.

3.2.3. Dissolution properties of the compacts

Solubility results of both compacts and of their corre sponding non compacted blends are shown in Fig. 7. Compression increases dissolution times, while prior gran ulation deactivates the product.

Both processes make the compact more difficult to dissolve without agitation: the solution conductivity only increases after 300 s only, when agitation is turned on. Compression increases dissolution times, six times for direct compression and twice for compaction after granulation. It is here not possible to evaluate here the effect of granulation on dissolution times, since the dissolution of the "initial blend for granulation" was not measured. What can be said is that the "initial blend for direct compression" dissolves three times faster in water than the granules mixed with metasilicate, when not compacted. Once compacted, the dissolution rates are identical or even faster for the granules and metasilicate. Compaction pressures considered here are rather high (20 kN) and could in part explain the long dissolution times. Additionally, it has been observed in another study that the presence of a nonionic emulsifier in the formulation forms a gel like film in contact with water, which renders the dissolution even more difficult. For a

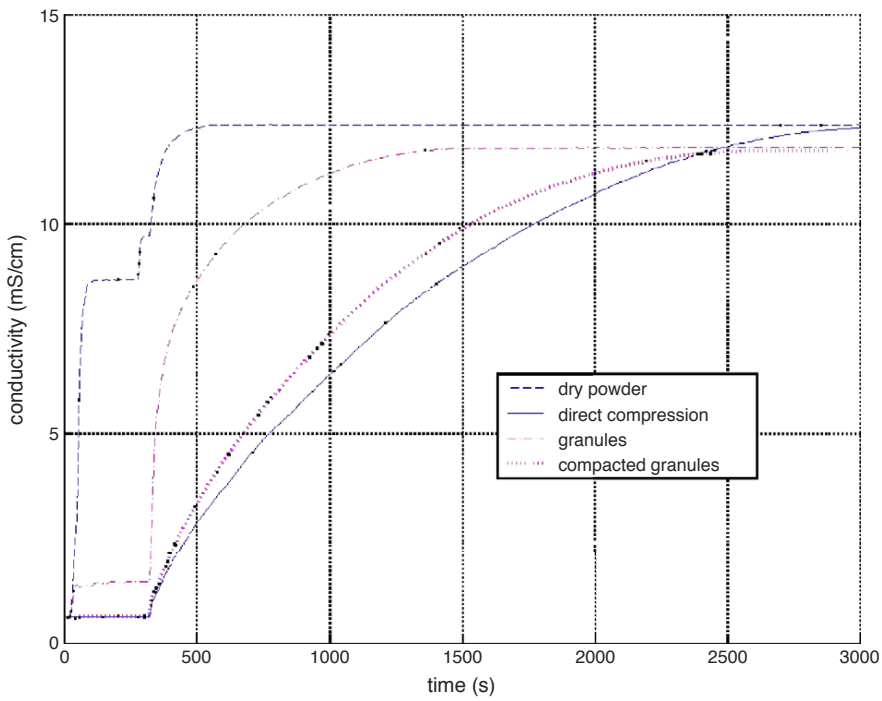

Fig. 7. Solubility of both compacts and their corresponding non-compacted blends.

good dissolution of the compact, water has to penetrate and/or dilute the substances progressively at the contact surface. This might be facilitated by the effect of water already involved in the previous granulation step.

One of the obvious effects of water in the granulation step is the decrease in conductivity for the product that has been granulated (end conductivity of 11.8 ± 0.1 mS/cm) compared to the blend for direct compression (end conductivity of 12.3 ± 0.1 mS/cm). This decrease of 4.4% in conductivity is probably due to chemical reactions between water and powdered raw materials. Among others, solidification by crystallization of salts, leading to local solid bridges, might be one of these reactions.

4. Conclusion

Two detergent powder processing methods have been investigated at laboratory scale: direct compression and wet high shear granulation with water as liquid binder, followed by compression. Angles and densities measurements on powder and granules show that granulation drastically improves flowability but slightly reduces compressibility. In the chosen conditions (device and formulation), the parameters to be fixed to obtain a narrow granule size distribution around 1 mm diameter are impeller speed (350 400 rpm), and liquid/solid ratio in between 0.12 and 0.15. High shear is necessary to disperse the liquid binder on the powder for good wetting and nucleation. According to measurements of granules densities and SEM image analysis, coalescence is the predominant growth mechanism if the saturation rate is high enough. The compression of granules containing 8.6% of water was compared to the direct compression of the dry powder (1.8% of water). It was observed that higher water content confers higher cohesion to the material and allows plastic deformations. Indeed, compacts made from granules are more mechanically strong, less friable and have a higher density. Fragmentation and granular rearrangement are the main mechanisms of dry powder compression molding, leading to weaker binding forces, and lower compact density. Granulation slightly deactivates the detergent formulation by reducing the conductivity of the final detergent solution, probably due to reactions of water with the different inorganic salts or surfactants. Finally, it was shown that compression increases dissolution time, this even more if no previous granulation was performed. In addition to slight deactivation, water involved during granulation may prepare the compact for disintegration and dissolution.

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