Powders surface formulation effect on powder rheological behaviors

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Résumé :

L'influence de la formulation des poudres sur leur rhéologie a été étudiée. Dans ce but, des billes de verre avec un diamètre moyen de 100 µm ont subi différentes préparations. Afin d'étudier l'influence de la composition de surface des particules, des traitements permettent de les rendre hydrophiles, hydrophobes ou d'ajouter un revètement de lactose. De plus, afin d'étudier l'influence de la composition du coeur des particules, des particules de lactose agglomérées d'environ 100 µm de diamètre moyenne ont également été produites par granulation humide à cisaillement élevé et controlé.

La granulométrie par diffraction laser a permis de déterminer la distribution en taille. L'aspect de la surface des particules des billes de contrôle , ainsi que des poudres de lactose agglomérées est visualisé par microscopie électronique. Les propriétés d'écoulement obtenues avec un rhéomètre à poudre FT4 ont montré que toutes les poudres sont dans la catégorie des poudres à écoulement facile. Les billes de verre hydrophobes présentent la plus grande fluidité et les billes de verre enrobées de lactose la plus faible. De plus, la viscosité apparente des poudres a été mesuré avec un rhéomètre utilisant une géométrie de Couette. Avec cette méthode, les billes de verre hydrophiles ont montré la fluidité la plus élevée et le lactose aggloméré la plus faible.

Abstract :

Influence of powders formulation on their rheology has been studied. With this purpose, one type of glass bead with median size of 100 µm has been implemented. In order to study the influence of surface composition, various surface treatments leading to hydrophilic, hydrophobic and lactose-coated surfaces were performed on glass beads. Moreover, in order to investigate the influence of powder core

composition, agglomerated lactose powders of circa 100 µm mean particle size were also produced by high-shear wet granulation and characterized.

Particle size distribution of control and surface-modified glass beads, as well as agglomerated lactose powders was determined by laser diffraction granulometry. Flow properties, which were characterized with a FT4 powder rheometer, showed that all powders are in the category of easy flowing powders. The hydrophobic and agglomerated lactose showed the highest and lowest flowability, respectively. Also a rheometer using a cylindrical Couette geometry has been implemented to study the flowability of powders on their apparent viscosity. In this case hydrophilic glass bead and agglomerated lactose showed highest and lowest flowability, respectively.

Key words: Flow properties, rheometry, powder surface formulation, agglomeration.

1 Introduction

The study and comparison of formulated powders are of a great interest as it can suggest solutions to improve the transport of powders. The flowability of glass beads was largely investigated in previous studies [1-2]. The dependency of powders flowability to the moisture [3] and formulation [4] is a well-known phenomenon. Depending on the humidity, the liquid bridge formation between the particles increases the cohesion of the powder for a given formulation. Thus powder flowability is expected to decrease [5]. Moisture sensitivity depends on the properties of the particles surface. To modify the sensitivity of the powder to the moisture, hydrophilic and hydrophobic treatments are performed. Lactose coating is also used to modify the particle surface. This treatment is sensitive to moisture but it modifies also the shape of the particles surface. Therefore, lactose coating may modify friction between particles. The friction between particles in granular materials is known that it influence particles flowability [6, 7]. In addition, in order to compare obtained results with the flowability of a real powder, agglomerated lactose powder with the same particle size was produced. It may present a different Young modulus than the core glass beads. The Young modulus influences the collision effect during the flow. Therefore, aforementioned treatments modify the interactions between particles, consequently powder flowability.

To evidence the effect of surface treatments and lactose agglomeration, particle size distributions were evaluated. Finally, the flowability of powders have been studied and compared by performing tests with a FT4 powder rheometer (Freeman Technology) [8] and rheometer Discovery HR3 [9, 10]. The FT4 powder rheometer provides comprehensive series of methods that allow powder behavior to be characterized, in this paper, rotational shear cell tests have been performed on the powders, shear cell test allowed to determine parameters linked to the flowability of powders in a high stress environment: cohesion and flow factor. Furthermore, rheometer Discovery HR3 has been used in order to obtain the flow curve of the powder samples. Rheometer Discovery HR3 [1, 9, 10] can operate in shear rate imposed state and gives wide range of data which makes us able to classify the powders. Then we compared the classification of powders in term of flowability based on the apparent viscosity of the powder with the results obtained with FT4.

2 Material and methods

Glass beads type S 90-150 µm (purchased from Sigmund Lindner GmbH, Germany) and monohydrate lactose powders (Granulac 200) with a median size of 32 µm (purchased from MEGGLE group WASSERBURGE, BG excipients & technology, Germany) were implemented in this study. Three types of glass bead surface formulation consisting of hydrophilic, hydrophobic and lactose coating have been performed. Sulfuric acid (Sigma-Aldrich, Germany), 1H,1H,2H,2H-Perfluorooctyltriethoxysilane (Sigma-Aldrich, Germany), hydrogen peroxide (VWR International S.A.S, France) and toluene (VWR International S.A.S, France) were utilized in formulation of hydrophilic and hydrophobic glass beads.

Hydrophilic surface treatment has been done with a mixture of sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2) with a ratio of 75/25 (mL/mL). Glass beads (50 g) were put in a beaker and immersed in sulfuric acid then hydrogen peroxide was gently added. The mixture was kept 4 h under extractor hood. The glass beads were filtered and washed with distilled water then they have been dried during 4 h at 70 °C. For preparing hydrophobic treatment [11], the hydrophilic treatment was first performed then toluene (500 mL) and after 1H,1H,2H,2H-perfluorooctyltriethoxysilane (2.5 g) were added on the beads and kept 72 h under extractor hood. Then the beads were filtered and washed two times with pure toluene and finally put under extractor hood during 24 h in order to be dried. For lactose coating, a lactose saturated solution [12] (composed of 100 mL distilled water and 18 g lactose) was prepared. Lactose powder was rehydrated with IKA RET basic IKAMAG safety control (product of Sigma-Aldrich, Germany) about 30 min at 300 rpm in ambient temperature. The lactose solution was added on glass beads (70 g) until covering them. After 30 min stirring, the mixture of saturated lactose with glass beads was dried in an oven (2 h at 70 °C). Finally, for lactose agglomeration [13], the lactose powder was agglomerated with a Mi-Pro 500 mL (product of Pro-C-epT, Belgium) and operating parameters were selected with the objective of obtaining 100 µm mean particle size. During agglomeration the water/powder ratio was 6 mL/50 g, stirring by 1000 rpm, duration of water addition was 3 min (water flow rate was 2 mL/min), a 2 min consolidation time was added and the chopper speed was 3000 rpm. Particles were dried at ambient conditions for one day.

2.1 Physical properties of powder

The measurement of particle size distribution of the powders has been done by Mastersizer 3000 laser granulometer (Malvern Instruments Ltd., Worcestershire, UK) supplied with Aero S dry dispersion unit and each tests have been repeated three times. Dispersion conditions were as follows: 1 bar, 100 % air pressure, 50 % feed rate and 4 mm hopper length. Particle size distributions were characterized by the median diameter D_{50} and the span. While the span represents the width of the particle size distribution and is calculated by the following formula:

$\text{Span} = (D_{90} - D_{10})/D_{50}$.

Where D_{50} is defined as the diameter where half of the population lies below this value. Similarly, 10 and 90 % of the distribution lies below the D_{10} and D_{90} respectively.

Also to check the efficiency of the surface treatment and lactose agglomeration properties, particle microstructure was imaged with a scanning electron microscope (S-240 Rustat Road, Cambridge, United Kingdom) operating at 3 kV acceleration voltage. Before analysis, samples were deposited on a carbon adhesive tab (EMS® 77825-12) at ambient temperature and coated with a mixture of gold/palladium for 100 s in a sputter coater (Polaron SC7640, Thermo VG Scientific, East Grinstead, England). The images were obtained at two magnifications: x 100 and x 600.

2.2 Flow properties of powder

The rotational shear cell tests on glass beads and agglomerated lactose powders were determined with a FT4 powder rheometer with standard methods also Rheometer Discovery HR3 has been used to compare obtained flow curves based on apparent viscosity with the results of FT4. Each tests for each powders repeated three times.

2.2.1 Rotational shear cell test

The flowability of powders by applying shear stress with a rotational shear head has been done with FT4 shear cell test. The shear cell itself was constituted of two overlaid glass cylinders of 25 mm diameter and 10 mL volume. After conditioning, powder was preconsolidated at 9 kPa normal stress. After that, decreasing normal stresses (σ) from 7 to 3 kPa by 1 kPa steps were successively applied and the shear stresses (τ) required to make the powder flow (i. e. to induce preconsolidated powder bed failure) were recorded. The yield locus approach was then applied by FT4 software to deduce the major principal stress (σ_1) and the unconfined yield strength (σ_c).
The flowability index *ff*, characterizing powder flowability was calculated with the following formula: $ff = \frac{\sigma_1}{\sigma_c}$.

According to Jenike [14], powders were classified as not flowing for $ff < 1$, very cohesive for $1 < ff < 2$, cohesive for $2 < ff < 4$, easy-flowing for $4 < ff < 10$ and free-flowing for $ff > 10$.

2.2.2 Rheometry with Discovery HR3

The rheological measurements have been done also by using an imposed shear-rate rheometer (Discovery HR3). The geometry which is used is six blades vane device (10 mm radius and 51 mm length) installed inside cylindrical Couette geometry; but only part of blade has been immersed inside the powder and the same mass of powder has been always used (17 g of glass bead and 9 g of agglomerated lactose) also the final height of the samples in the cell have been checked to determine the volume fraction of the powders and then the experiments have been carried out by imposing steady angular velocity. Enough time has been waited for each value of the angular velocity to confirm reaching stationary state. A detailed description of the calibration procedure and the equipment can be found in literature [9,10].

3 Results and discussion

Fig 1 is representation of size distribution of control, hydrophilic, hydrophobic, lactose coated glass beads and agglomerated lactose powders. Hydrophilic and hydrophobic surface treatments did not have any influence on the particle size distribution while agglomerated lactose powders and lactose-coated glass beads presented similar mean particle size but wider span than the other samples, meaning that lactose coating modified the surface of glass beads, making them prone to agglomeration and attrition (Table 1).

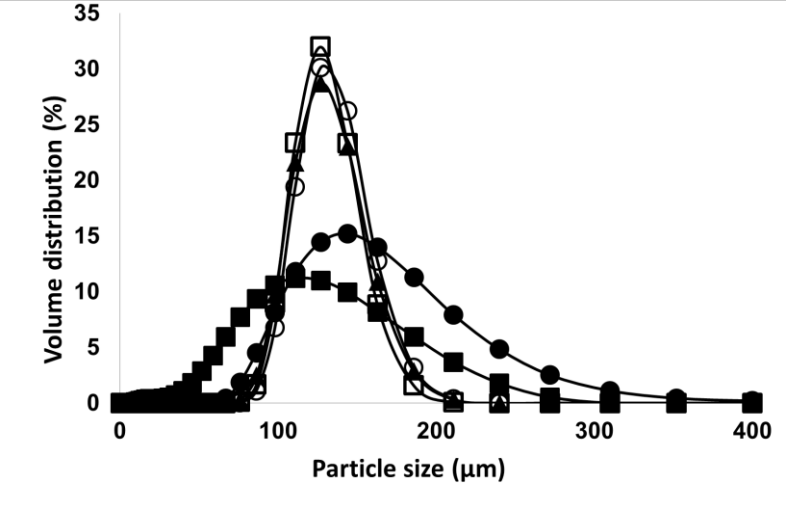

Figure 1. Particle size distributions of investigated powders with 100 µm mean sizes. *Full triangles: control glass beads, empty circles: hydrophilic glass beads, empty squares: hydrophobic glass beads, full circles: lactose-coated glass beads, full squares: agglomerated lactose.*

Table 1. *Granulometric parameters of investigated samples*

Powders	D_{50} (µm)	Span
Control glass beads	136.66±0.66	0.44±0.02
Hydrophilic glass beads	135.00±0.57	0.40±0.01
Hydrophobic glass beads	137.00±0.81	0.41±0.01
Lactose coated glass beads	155.00±3.00	0.92±0.09
Agglomerated lactose powders	113.00±1.00	1.18±0.00

Furthermore, particle morphology and surface appearance after surface treatment were imaged by SEM (Fig 2). Surface microstructure of hydrophilic and hydrophobic glass beads was comparable to control glass beads meaning that chemical treatment did not modify surface structure, but lactose-coated glass beads were a little larger and their surface was wrinkled.
SEM permitted to confirm the particle size polydispersity evidenced by laser granulometry for lactose-coated and agglomerated lactose samples.

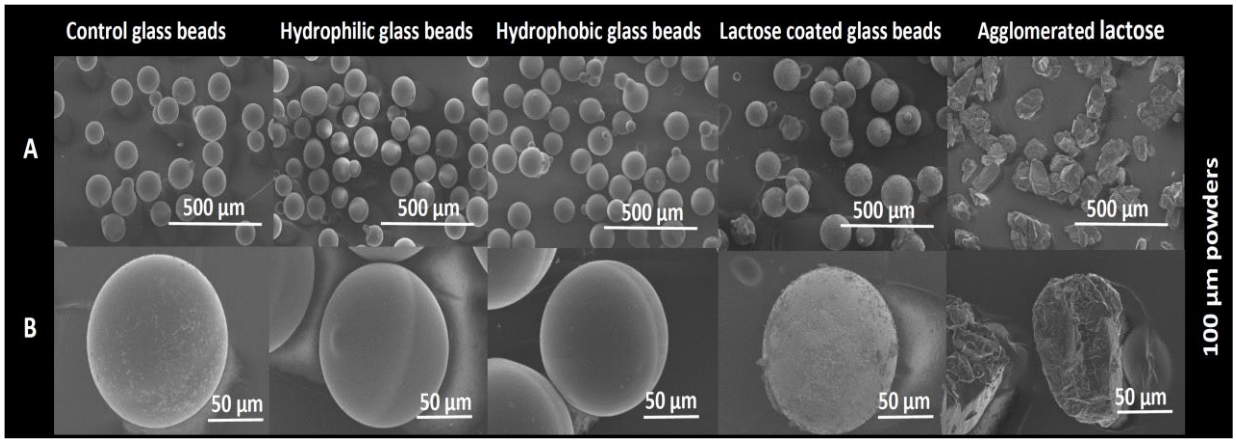

Figure 2. SEM images of investigated powders with the magnification of: x 100 (A) and x 600 (B).

Fig 3 shows the evolution of shear stress recorded at variable normal stress from 3 to 7 kPa at 9 kPa pre-shear stress for investigated samples. In general, the higher the curve on the diagram (i.e. the higher the incipient shear stress measured at a given shear rate) means the poorer flow properties [9, 15]; therefore investigated

powders can be ranked according to their flowability in shear stress conditions as: hydrophobic glass beads ≈ control glass beads > hydrophilic glass beads > lactose-coated glass beads > agglomerated lactose powders. All powders exhibited low cohesion values, consistently with good flowing properties; cohesion increased in following order: control glass beads ≈ hydrophobic glass beads < hydrophilic glass beads < lactose-coated glass beads < agglomerated lactose powders (see table 2). Also, *ff* values showed that all powders could be sorted in the "free-flowing" category, denoting their excellent flowing properties, as expected for such particles. According to *ff* values, powder flowability should be classified in the following order: control glass beads ≈ hydrophobic glass beads > hydrophilic glass beads > lactose coated glass beads > agglomerated lactose powders.

Table 2 *Stability and flowing parameters (derived from the shear cell test)*

Powders	**Cohesion (kPa)**	**ff (−)**
Control glass beads	0.20±0.00	19.76±0.81
Hydrophilic glass beads	0.27±0.02	17.27±1.06
Hydrophobic glass beads	0.20±0.01	19.74±1.66
Lactose-coated glass beads	0.31±0.03	13.44±1.21
Agglomerated lactose powder	0.42±0.06	10.01±1.44

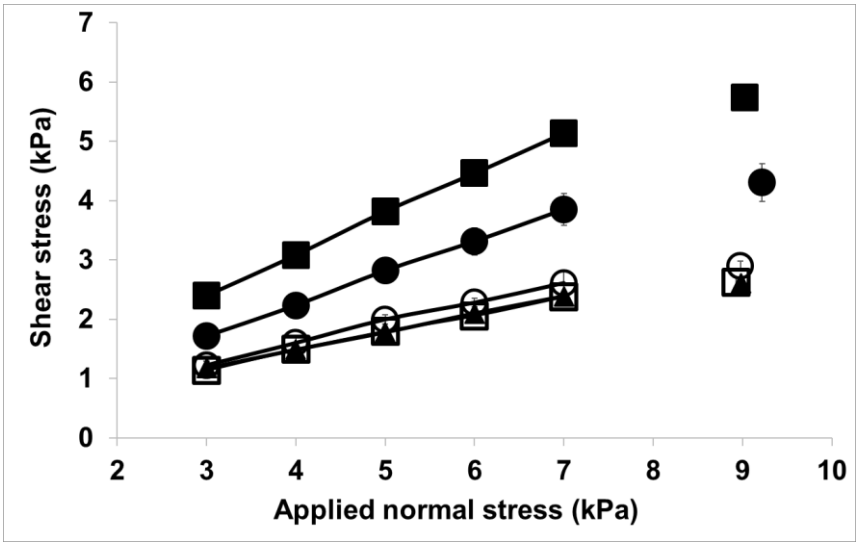

Figure 3. Evolution of shear stress with applied normal stress after pre-shear at 9 kPa with FT4. Error bars represent standard errors; some were not visible as the size was inferior than marker size. Full triangles: control glass beads, empty circles: hydrophilic glass beads, empty squares: hydrophobic glass beads, full circles: lactose-coated glass beads, full squares: agglomerated lactose.

Fig 4 shows the evolution of shear stress versus shear rate for glass beads (control, hydrophilic, hydrophobic, lactose coated) and agglomerated lactose powders which have been measured with rheometer discovery HR3. The data points are obtained by imposing angular velocity from 0.1 rad/s to 30 rad/s. Also only 1/3 of height of blade has been immersed inside the powders since by filling full height, the blade was not able to turn inside the powders, in low angular velocities. In general higher the cure means high shear stress required to let the powder to be motion consequently less flowability [1, 14], so based on this criteria it seems that agglomerated lactose powder showed less flowability than the other powders however hydrophilic glass bead, hydrophobic glass bead and control glass bead have very close flowability to each other while lactose coated glass bead has a flowability between agglomerated lactose and those three formulated powders. In general, hydrophilic glass bead showed highest and agglomerated lactose lowest flowability, respectively.

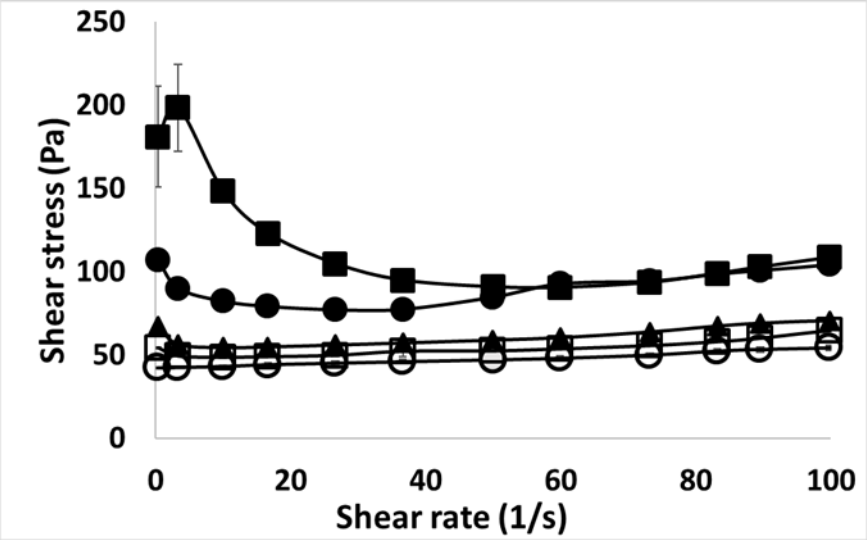

Figure 4. Evolution of shear stress with respect to the shear rate for different values of imposed angular velocity with the rheometer discovery HR3; Error bars represent standard errors; some were not visible as their size was inferior than marker size. Full triangles: control glass beads, empty circles: hydrophilic glass beads, empty squares: hydrophobic glass beads, full circles: lactose-coated glass beads, full squares: agglomerated lactose

4 Conclusion

The evaluation of the influence of chemical surface treatment on the powder flowability was the main objective of this study. Therefore, control glass beads were compared with surface-treated glass beads (hydrophilic, hydrophobic, lactose-coated) and agglomerated lactose powders. The particle size distribution evidenced that control, hydrophilic and hydrophobic glass beads did not differ in their particle size distribution, while agglomerated lactose powders and lactose coated glass beads presented similar mean particle size but a wider size distribution. According to the shear cell test by FT4 a classification of followability of powders in decreasing order is as follow: hydrophobic glass beads ≈ control glass beads > hydrophilic glass beads > lactose-coated glass beads > agglomerated lactose powders. However based on the rheomtery with Discovery the classification of powders flowability in decreasing order is as follow hydrophilic glass beads > hydrophobic glass beads > control glass beads > lactose-coated glass beads > agglomerated lactose powders; taking into account that same height of powders is used for the different powders meaning that the normal stress influenced the agglomerated lactose different than the powders with glass core. In sum up, however different classifications have been obtained for two different tests but hydrophilic glass bead, hydrophobic glass bead and control glass bead had very close flowabilities in both tests while agglomerated lactose showed lowest flowability in both tests.

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6 References

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