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Modifications of powders properties by dry-coating: some examples of processes and products characteristics

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Abstract
Dry-coating appears to be an interesting way to create new composite materials in various application areas, avoiding the use of solvents involved in traditional processes, like granulation. Moreover, dry coating processes can be performed on smaller particles sizes.
Typical applications include, but are not limited to, altering flowability, solubility, dispersibility, wettability (hydrophilic/hydrophobic properties), electric, electrostatic, magnetic, optical, color, flavor, shape, etc. Particles with relatively large particle size (host particles, 1-500 µm) can be mechanically coated with fine particles (guest particles, 0,1-50 µm) in order to create new functionality or to improve their initial characteristics.

In this study we present results obtained with various products and in particular more accurately in the case of silica host particles coated by magnesium stearate using two processes: the Hybridizer NSH0 of the Nara Machinery company and the Cyclomix of Hosokawa company.

In this paper we describe the experimental investigation of an application of dry coating technique to change the surface properties of silica gel particles (d_{50} = 55 µm) coated with different mass ratio of magnesium stearate (MgSt; d_{50} = 4,6 µm): 1%, 5% and 15%.

The products properties were characterised though different methods: particles size distribution (in order to examine the adhesion quality of the fine particles on host particles), flowability, wettability, Atomic Force Microscopy (AFM), and Electron Microscopy (ESEM).

The flowability of the samples was characterized by measurements of the tapped and aerated densities. It has been shown in particular that the flowability of silica gel treated with and without MgSt in Hybridizer was not significantly affected and remained good. The wettability of silica gel was determined by measurements of the contact angle between the water drop and the powder bed prepared for each sample. The results obtained have shown that the coating of silica gel powder by hydrophobic magnesium stearate, can improve its hydrophobic properties.

1- Introduction

Dry-coating processes (Figure n°1) may be used in order to formulate new composite-particles with designed end-use properties. They have found an increasing interest in the two last decade with the emergence of the environmental preoccupations, and with the development of the use smaller composite particles and more generally with the use of very fine powders.

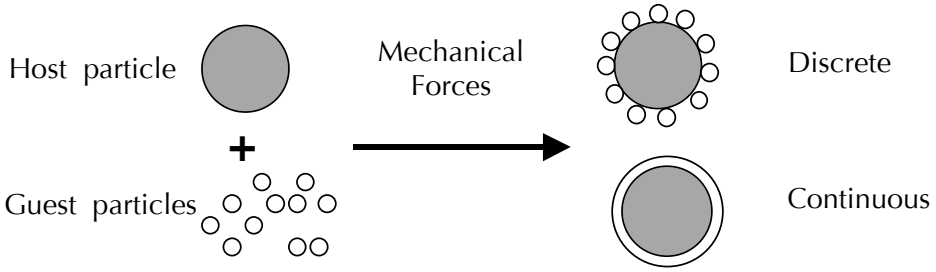


Figure n°1 : dry coating, the principle [1-2]

For example, decreasing the particles size, the increase of the powders cohesivity may make them more and more difficult to handle (for example decreased flowability in silos discharge, and in pneumatic transport). The possibility of fixing theses small particles on bigger ones in order to facilitate their manipulation, may be offered by co-grinding or dry-coating processes. After various trials on pharmaceutical powders (actives and excipients) showing the diversity of behaviour of the powders couples, and the difficulties to find pertinent characterisation techniques to study the processes and the quality of the coating, we decided to focus on a model couple to develop the characterisation approaches and the process understanding.

In this paper we describe an experimental investigation of an application of dry coating technique to change the surface properties of silica particles coated with different weight ratio of magnesium stearate by dry-coating using tow processes: The Hybridizer supplied by Nara Machinery company and the Cyclomix from the Hosokawa-Micron Company. Several lab techniques were used to characterize the physico-chemical properties of the uncoated and coated particles.

2 - Material and methods

2-1 Powders

Silica gel

Silica gel powder supplied by Merck has been used as the host particles. This powder has a hydrophilic porous structure, and its particles are irregularly shaped with a notable the surface roughness (Figure n° 2). The main characteristics (diameter, density and specific surface area) are summarized in Table n°1.

Magnesium stearate

Magnesium stearate (MgSt) supplied by Chimiray is a hydrophobic powder that has been chosen as guest particles in order to use its hydrophobic properties for changing the Silica gel surface behaviour.

The MgSt is a fine (see Table n°1 for the main characteristics), white, greasy and cohesive powder widely used in pharmaceutical formulation as a lubricant. Observation by ESEM (Figure n°3) showed a wide distribution of size and shape, including needle and plate like particles.

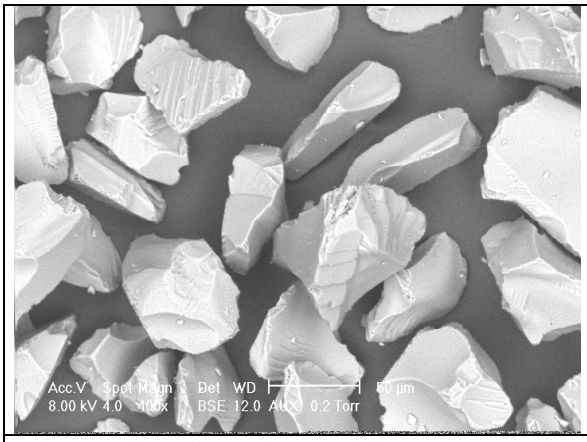


Figure n°2 : ESEM picture of Silica gel as received

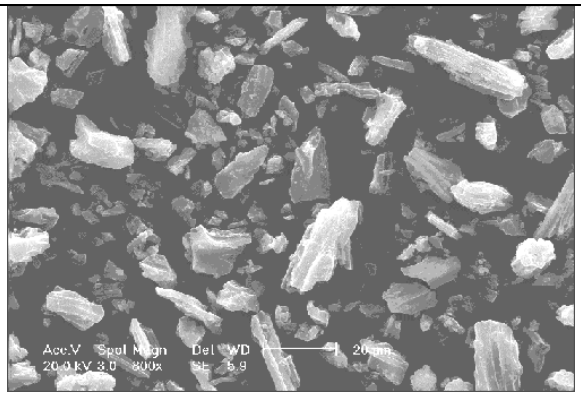


Figure n°3: ESEM picture of StMg as received

Table n°1: Main properties of the host and guest particles

Particles	Size (d_{50}) (µm) (Mastersizer 2000)	True density (ρ) (g/cm^3) (Helium Pycnometer)	Specific surface area (S_{BET}) (m^2/g) (Micromeritics ASAP 2010)
Silica gel (host)	55 (D_{host})	2.07 (ρ_{host})	475
MgSt (guest)	5 (d_{guest})	1.04 (ρ_{guest})	7.7

2-2 Processes

Two different processes were used to carry out the experiments:
The first one, the Hybridizer of Nara Machinery (Figure n°4) consists of a rotor (12 cm in diameter) with six blades, a cooled stator and a powder re-circulation pipe. The rotor's speed may be adjusted up to 16000 rpm. Host and guest particles (about 30 g) are simultaneously processed in the rotor's zone and re-circulated in the machine through the recycle tube as described in various previous works [2-7]. In this device, particles coating results from the embedding or filming of the guest particles onto the surface of the host particles by high impaction forces and the heat of friction. In this case, dry-coating appears as a consequence of a co-grinding treatment in a batch hammer mill process.

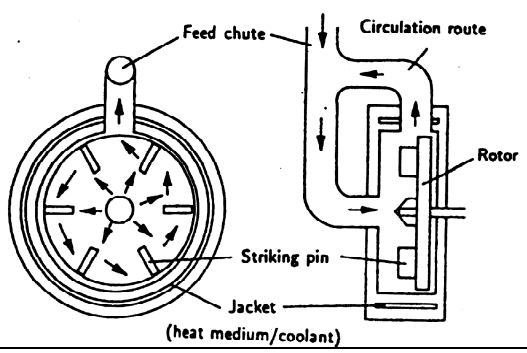


Figure n° 4: schematic diagram of the Hybridizer Nara [3]

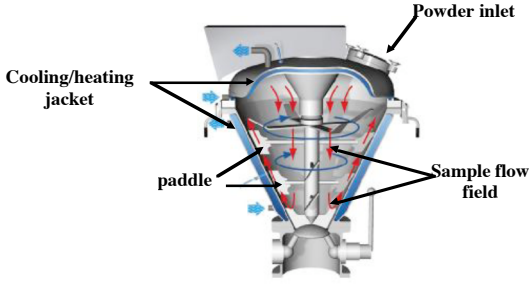


Figure n° 5: Diagram of a Cyclomix high shear mixer

The second process used for this study is a Cyclomix, a conical high shear mixer with a 1L capacity provided by Hosokawa Micron and previously described in different works [8-9]. Its mixing device has four pairs of flat-bladed impellers set in series on an axially located shaft that has a high rotation speed. This eliminates seals and bearings from the product zone. This shaft is fitted with paddle-shaped mixing elements, which rotate close to the inner vessel wall Figure n°5 shows a diagram of the action of a Cyclomix mixer. Its working principle differs significanly from the classical mixing apparatus and from other devices used for dry powder coating owing to the specific interaction between mixing element and vessel wall. The powder (host and guest particles) is loaded into the conical mixing vessel from the top; the degree of filling can range between 30 and 100%. The high-speed of rotation (up to 2500 rpm) of the paddles and the conical shape of the vessel induce a forced circulation of the product from the bottom to the upper zone of the vessel. Upon reaching the top, the product flows downwards into the centre of the vessel. This flow pattern results in fast macro-mixing. During the upward motion, the particles are accelerated by the paddles and intensively mixed by friction with vessel walls. The operating conditions used in all experiments presented here are 80% filling and 1500 rpm for 5 min.

2-3 Analytical techniques

One of the first difficulties in this kind of transformation is to obtain a good and pertinent characterisation of the product relative to the wanted end use property. In the various cases observed in the laboratory this characterisation requires a cross interpretation of various techniques.

In order to quantify the amount of MgSt in the mixtures after treatment, analysis by **Differential Scanning Calorimetry (DSC) coupled with termogravimetry (TG) (TG-DSC 111**) have been performed under nitrogen flow for a temperature ranging between 20-600°C (degradation of magnesium stearate occurs at approximately 600°C) and heating flow of 5°C/min. The amount of remaining MgSt is then quantified by measuring the weight loss characteristic of this ingredient.

The surface morphology and particle shape of the coated products and of the particles fed in the processes were observed by **environmental scanning electron microscopy (ESEM)**.

Atomic Force Microscopy (AFM) has been used to characterise the topography of the coated particles and the interactions between host and guest particles. They were carried out with a scanning probe microscope Multimode Nanoscope IIIA (Digital Instruments/Veeco Metrology Group). The measurements were performed at room temperature in tapping mode with a phosphorus (n) doped Si probe (stiffness 40 $N.m^{-1}$). Height, amplitude and phase images were simultaneously recorded for each sample. Beyond the classical height imaging, the phase contrast mode is quite efficient to exhibit the main surface property differences between the silica gel and MgSt. For the coated particles, the part of the image characterized by high phase angles can be attributed to the presence of MgSt layers on the surface of silica gel.

To evaluate the strength of host-guest interactions a Standard **Malvern Mastersizer with dry powder feed** has been used. In this apparatus powder de-agglomeration is controlled by adjusting the dispersing air pressure [10]. Five dispersing air pressures were used: 0.5; 1.5; 2.5; 3.5 and the maximum pressure of 4 bars.

The tapped density tester has been used to study the flowabilty of the uncoated and coated samples. The tapped density is achieved by mechanically tapping a measuring cylinder containing a powder sample. After observing the initial volume, the cylinder is mechanically tapped, and volume readings are taken until little volume change is observed. The flow properties of the uncoated and coated powders were evaluated by the Carr's flowabillity index (I_{Carr}) and Hausner's ratio ($R_{Haussner}$).

The wettability has been studied by **the sessile drop method** [11]. A 10 µl water drop is deposited on the surface of a powder bed prepared for each sample. The contact angle is then measured observing the profile of the drop pictures.

3 Results and discussion

3-1 Experimental yield - Ratio MgSt/Silicagel in the products

During the experiments carried out in the Hybridizer, a part of the feed powder stayed stuck on the device's wall and the amount of collected product was also lower than the quantity introduced at the beginning of the experiment. In particular, a significant deposit of magnesium stearate on the surface of the rotor and of the blades was observed after any experiments.

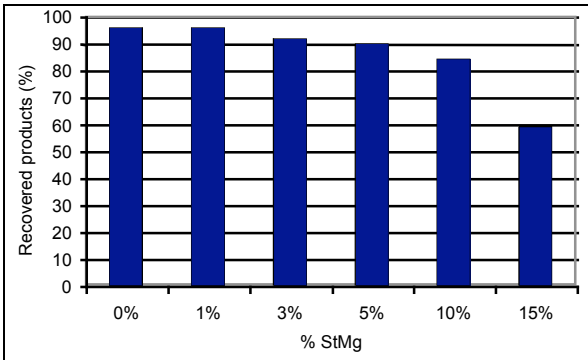


Fig n°6: Experimental yield for Hybridizer experiments

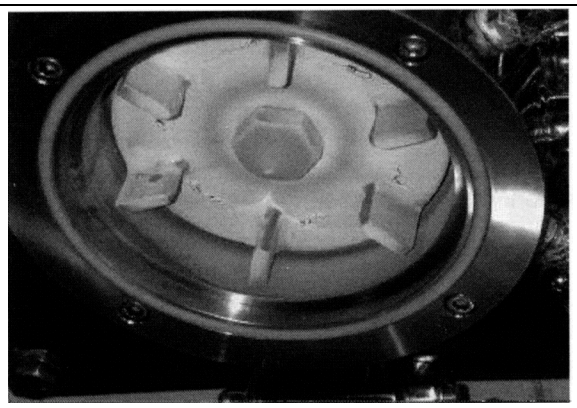


Fig n°7: The hybridizer's rotor after experiment

A segregation phenomena occurs in the hybridizer process and a significant part of the fed particles become stuck on the walls of the process chamber (Fig n°7) after the recovering step of the product.

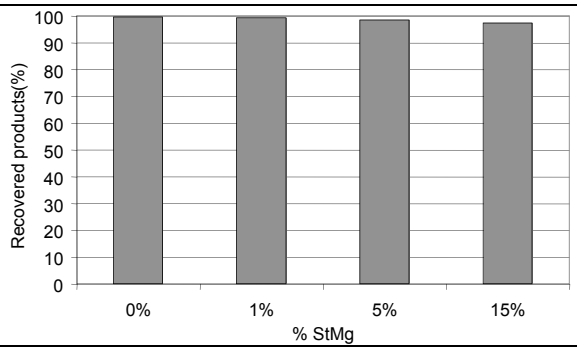


Fig n°8 Experimental yield for Cyclomix experiments

It is therefore necessary to quantify the real amount of MgSt remaining in the product. Figure n° 9 shows the results obtained after TG/DSC analysis.

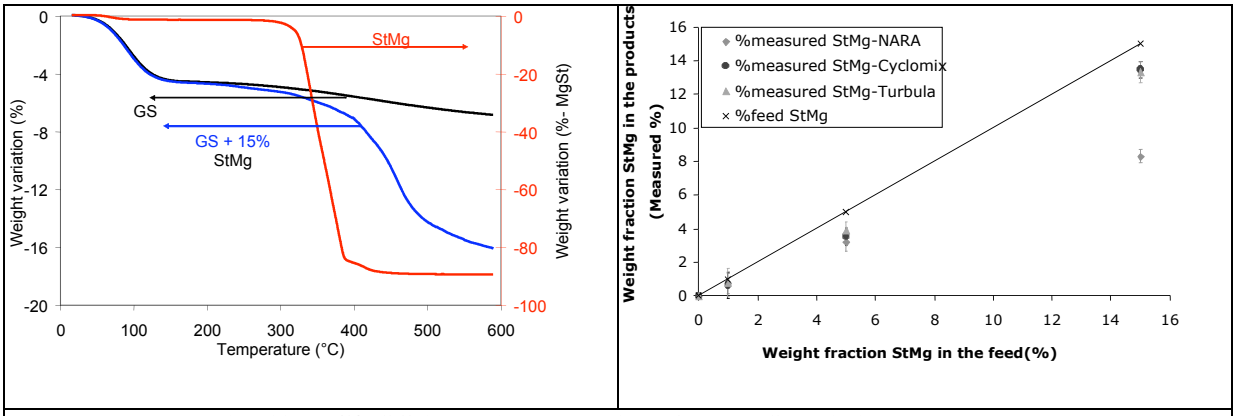
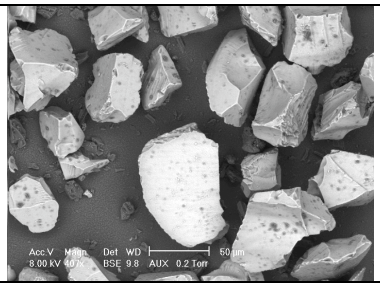


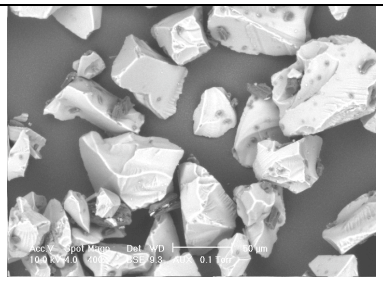
Fig n°9 : TG/DSC Analysis : evaluation of the MgSt ratio in the products

3-2 Shape and surface morphology (ESEM)

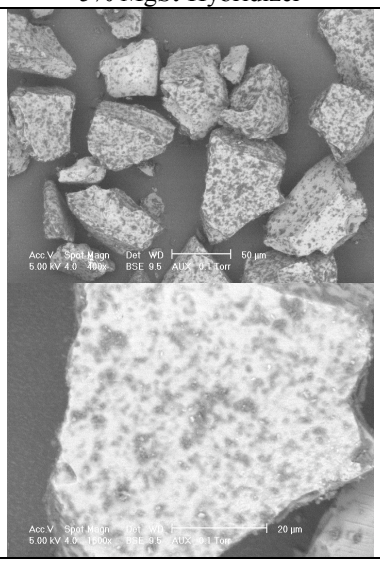
The processed particles were immediately after treatment observed with the ESEM technique. For both 5% and 15% mixtures, we can observe in Fig. n°10 a discrete distribution of the MgSt particles on the Silica gel surface with a better coverage in the second case. More over the hybridizer treatment leads to a better smearing and softening of the guest particles.



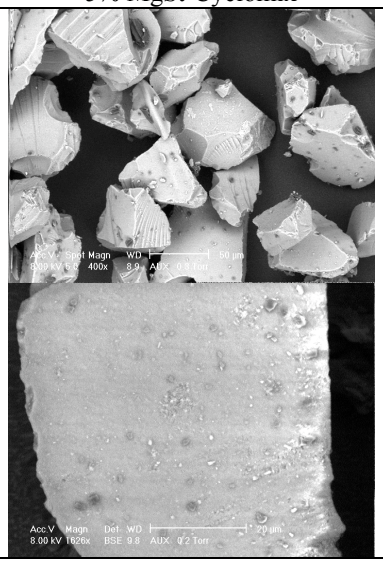
5% MgSt-Hybridizer



5% MgSt-Cyclomix



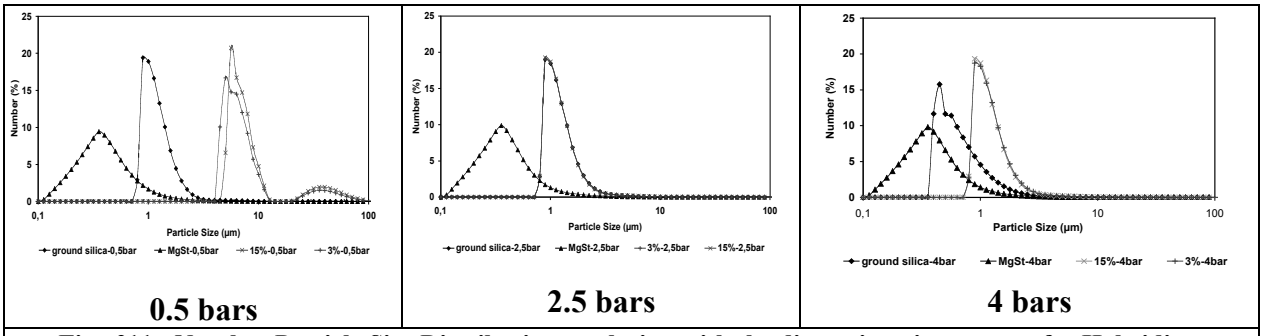
15% MgSt-Hybridizer



15% MgSt-Cyclomix

Fig n°10: :ESEM pictures of coated products

3-3 Coating strength by Particle size analysis



0.5 bars | **2.5 bars** | **4 bars**

Fig n°11 : Number Particle Size Distribution, evolution with the dispersing air pressure for Hybridizer experiments

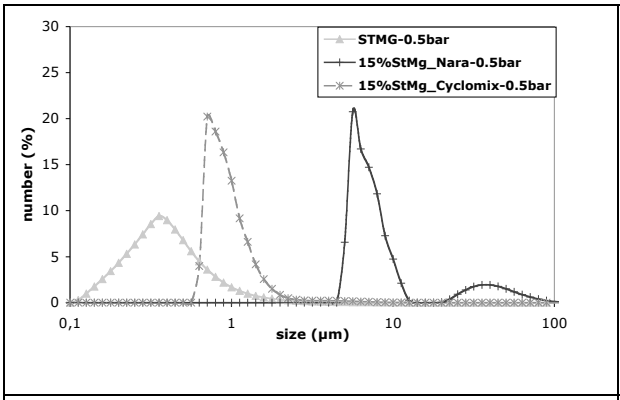


Fig n°12 : Hybridizer/Cyclomix, comparison of Number Particle Size Distribution at 0.5 bars dispersing air pressure

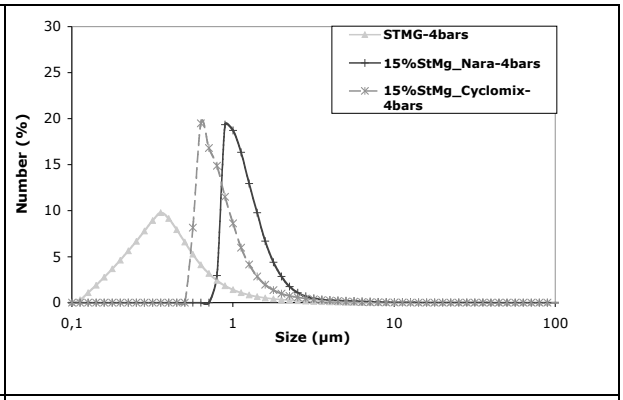
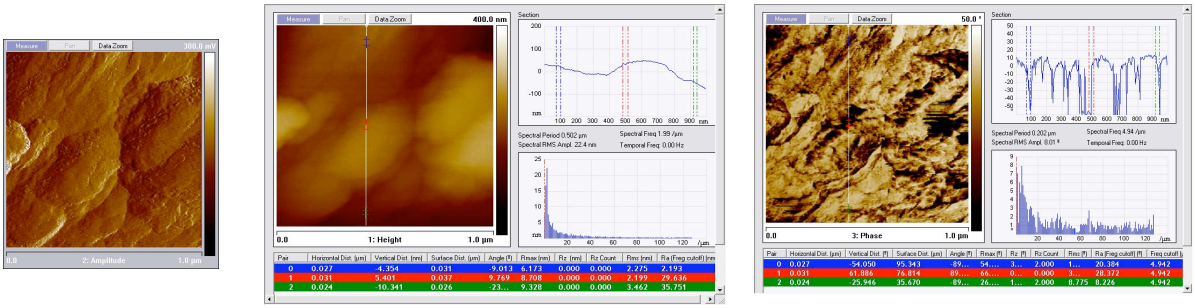


Fig n°13: Hybridizer/Cyclomix, comparison of Number Particle Size Distribution at 4 bars dispersing air pressure

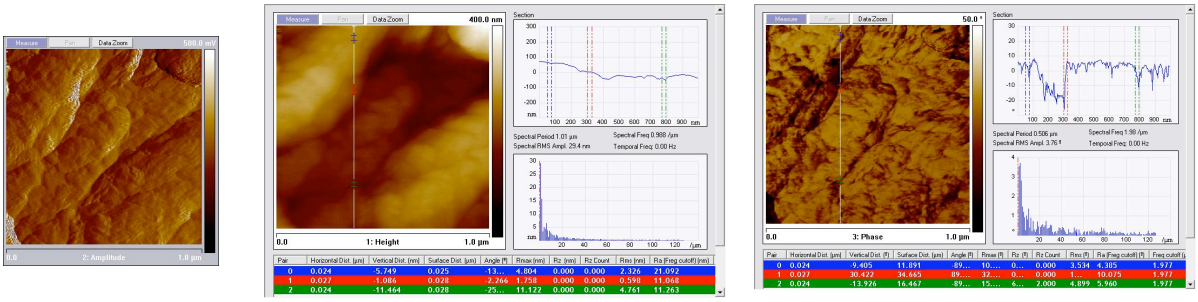
At very low dispersing air pressure the products observed show the presence of silica-silica agglomerates (Fig 11 and 12). For an air pressure of 2.5 bars (Fig 11) a de-agglomeration of silica-silica agglomerates is observed. Even with a 4 bar (Fig 11 and 13) dispersing air pressure no detachment of MgSt has been observed. In this case the interactions between host and guest particles are found to be strong.

3-4 Surface covering (AFM)

AFM analysis has been perform in order to understand how the hybridizer process allows obtaining a discrete, but uniform dispersion of the MgSt particles. Phase and Height images have been simultaneously recorded in tapping mode with phosphorus (n) doped Si probes (stiffness 3 Nm^{-1}) and gave an estimation of the thickness of the MgSt coating. In Fig°14 the first series shows the topography of MgST coated zone (dephasing approximately 50° as for MgSt alone) and the second series is an example of less coated zone with pure silica and any localised StMg coating parts (dephasing approximately 10°-30°)



Picture obtained on a coated particle with dephasing about 25° to 60°



Picture obtained on a coated particle with dephasing about 10° to 30°

Figure n°14 : analysis of height and phase profiles on tow sections (1x1 µm^2) of tow particles Silica Gel coated with 15% MgST.

In order to obtain a better characterisation of the coating, the processed particles were observed with the AFM technique using a probe equipped with a MgST particle. In these experiments, the interaction forces between the material stuck on the cantilever (Magnesium Stearate MS) and the surface of the composite material (Silica Gel SG or Magnesium Stearate MS), have been determined at different sites of the surface. Figure n° 15 shows the results obtained with samples of pure silica gel, of particles treated with different ratio of MgSt, and of pure MgSt. The higher is the proportion of MgSt, the larger is the distribution curve with higher interaction forces, whereas for a pure silica gel surface, this distribution curve has a narrow peak in the range of weak forces values. As observed in Fig n°15 the values observed for MgST/MgST interaction forces were in the range 50-150 nN whereas MgSt/Silica gel interaction forces were in the range 0-20 nN These distributions curves and the mean value f of the forces, f0 obtained for MS-GS interactions or f1 for MS-MS interactions have been established and the experimental curve showing the evolution of f versus w (weight ratio of MgST) has been derived. A modelling of the surface coverage versus MS amount is actually in elaboration.

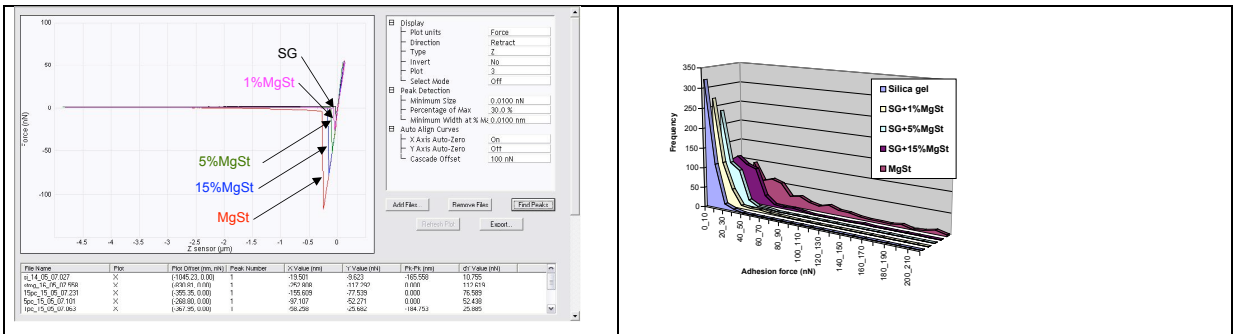


Fig n°15: AFM analysis :Influence of the coating on interaction forces with a MgSt probe

3-5 Flowability (Volumenometer – tapped density)

Table n°2 resumes the main characteristics of Silica Gel and Magnesium Stearate as received in terms of flowability evaluated with densities measurements.

Table n°2: Carr Index , Haussner Ratio and flowability of pure Silica Gel and Magnesium Stearate

Products as received	I_{Carr}	$R_{Haussner}$	Flowability
Silica gel	15.22	1.18	good
MgSt	34.10	1.52	bad

Tables n°3 and 4 show for both apparatus theses same characteristics after processing for pure Silica Gel or for mixture with 5% MgSt and 15% MgSt. In the case of pure Silica Gel or of the 5% MgSt mixture, the products treated with the hybridizer remains with a good flowability whereas those processed in the Cyclomix show a decrease of this property. This trend is confirmed for the 15%MgSt mixture that has a poor flowability after treatment in the Hybridizer and a bad flowability after treatment in the Cyclomix.

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Table n°3: Carr Index and Haussner Ratio obtained for coated products with the Hybridizer and the Cyclomix

	Hybridizer		Cyclomix	
	I_{Carr}	$R_{Haussner}$	I_{Carr}	$R_{Haussner}$
Silica gel	15.24	1.18	18.45	1.23
Silicagel+5%MgSt	17.6	1.22	20.96	1.27
Silicagel+15%MgSt	18.22	1.22	21.21	1.27

Table 4: flowability of the products coated with the Hybridizer and with tthe Cyclomix

	Hybridizer	Cyclomix
Silica gel	good	poor
Silicagel+5%MgSt	good	poor
Silicagel+15%MgSt	poor	Bad

3-6 Wettability (water drop)

As shown in Fig n° 16 a water drop deposited on bed of silicagel particles is instantaneously absorbed consequently to the High hydrophilicity of this material.

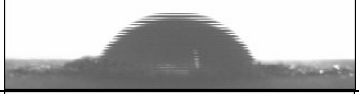
0s (initial drop)			
1s later…the drop is absorbed in the powder bed			

Fig n°16: Wettability of Silica gel powder before coating

After a MgSt dry-coating treatment, both with Hybridizer and Cyclomix, this property is significantly altered and the drop (Figure n°17) remains on the particles bed more than one minute, that proves the efficiency of these processes in terms of coating for surface properties modification

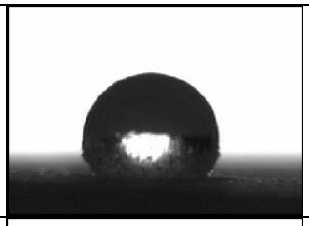
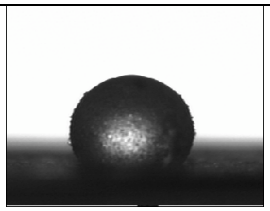
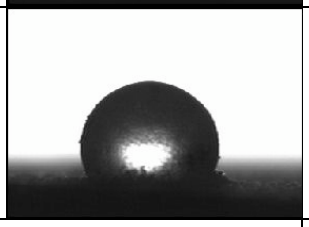
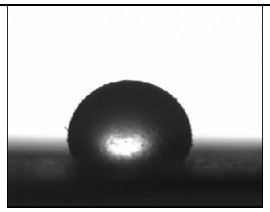
Initial drop (0 s)		
After 1min		
	5% MgSt	**15%MgSt**

Fig n°17: Wettability of coated Silica gel particles

4 Conclusion

Dry-coating of Silica gel particles has been carried out with two different processes and varying the guest particles amount. The coating quality and its influence on properties of the coated product were evaluated through various characterisation methods. In particular the use of AFM analysis seems to be a promising technique in order to estimate the proportion of coated surface an interesting way to elaborate a model describing the relationship between the coating quality and the amount of magnesium stearate.

5 References

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