DRY COATING PROCESS USING POLYSACCHARIDES IN A PAN COATING SYSTEM

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Abstract

Coating of inert pellets of microcrystalline cellulose with modified starches by the dry powder coating technique was investigated, as an alternative to organic- and aqueous-based coatings.

The coating process has been conducted in a Pan coater and the coating formulation is divided into two components, a powder polymer and a liquid plasticizer.

The experiments carried out have shown high coating process efficiency. The best coating results were obtained using particles smaller than 50μm and having a polygonal shape. The dry coating technique has shown a reduction of processing time compared to standard coating techniques.

SEM analysis has shown uniform coating shell thickness onto pellets without presence of coalescences in processes conducted at room temperature.

Confocal Laser Scanning Microscopy (CLSM) was used to characterize the dry coated particles in order to measure coating quality and thickness. A protocol for dry coated pellets characterization has been set up. Results obtained by CLSM have demonstrated an effective increase in coating thickness with increasing coating level.

1. INTRODUCTION

The principle of coating particles is used in the pharmaceutical field to enhance drug stability, avoiding drug degradation by oxygen, moisture, light and taste masking.

In the food industry too, the coating technology is frequently used to separate ingredients from their environment (water, acid, oxygen, other food ingredients), which may be detrimental to the uncoated material or the food itself. It could be used to stabilize ingredients during processing (heat, pressure, moisture), to impart controlled release (during processing, storage or consumption), to change physical characteristics of the original material by reducing the hygroscopicity or improve flowability and compression properties, reducing dustiness or modifying density [1,2].

In the traditional coating, the process consists of spraying a coating material solution on pellets. In case of organic-solvent based process, solvent has to be recovered to avoid pollution, leading to an important overcost. Coating processes with aqueous dispersions are time and energy consuming [3] as a result of the low concentration of coating polymer and large amounts of water to be evaporated.

In the last decade coating with polymer powders has been studied as an innovative technology and alternative to the traditional coating with an aqueous polymer dispersion or organic polymer solution.

Dry particle coating consists of coating large particles (core material or host) with fine powder (guest). The adhesion of these guest particles is made using a mechano-chemical treatment or using a plasticizer. The plasticizer method is particularly when coating host particles that are relatively soft and very sensitive to heat and can be deformed by severe mechanical forces [5,6,7]. Compared to solvent and water based coating the dry coating method is favourable regarding environmental friendliness, safety and cost.

The present contribution wishes to provide preliminary results to apply dry coating in the food and pharmaceutical field. More generally, the aim of this study is to obtain host particles coated with polysaccharides by dry coating process in a pan coating reactor.

2. MATERIALS & METHODS

2.1 Materials

Host particles: Microcrystalline Cellulose pellets (CELLETS®1000-1400µm, IPC Process-Center GmbH & Co. KG, Dresden, Germany) as inert support.
Guest powder particles: Starch octenyle succinate (E1451), Tapioca Dextrin (National Starch, Düsseldorf, Germany), Malto-dextrin, Aluminium starch octenyle succinate and Octenyl succinate dextrin of waxy maize (Roquette, Lestrem, France).
Plasticizer: Triethyl citrate (TEC, Merck KGaA, Darmstadt, Germany), Glycerol (Acros Organics, Geel, Belgium).
Equipments: A Pan Coater device (prototype designed and manufactured in our laboratory), 40cm in diameter and 25cm in width, was used. An air compressed spray nozzle, with a range between 0-3 bars, was fixed at 20cm from the coater surface (Fig.1).

2.2 Methods

Experimental procedure: 400g of cellulose pellets were charged on a pan coater reactor (Fig.1). The rotational speed of reactor was fixed at 35 rpm. Plasticizer and polymer powder are simultaneously charged in the reactor chamber, respectively, by an air compressed atomisation nozzle at rate of 2 ml/min and by a feeding at rate of 5 g/min. The atomization pressure was set to 0,3 bars.

Polymer analysis: The particle size of the polymer powders was determined by laser light diffraction (Mastersizer, Malvern, United Kingdom). The relative frequency of the diameter of the particles was shown with the calculation based on volume distribution. The value of the median is the average of three measurements.

Coating variables: The coating efficiency and coating level were calculated by the follow relations:

$$\textbf{Coating process Efficiency (\%)} = \frac{M_{cP} - M_{uP}}{M_{Poly} + M_{Plas}} \qquad \textbf{Coating Level (\%)} = \frac{M_{cP} - M_{uP}}{M_{uP}}$$

where M_{cP} and M_{uP} are respectively the weight of coated and uncoated pellets, M_{Poly} is the amount of coating polymer and M_{Plas} is the amount of plasticizer).
The coating level is the weight of the polymer powder and plasticizer (M_{cP}-M_{uP}) divided by the weight of uncoated pellets (M_{uP}).

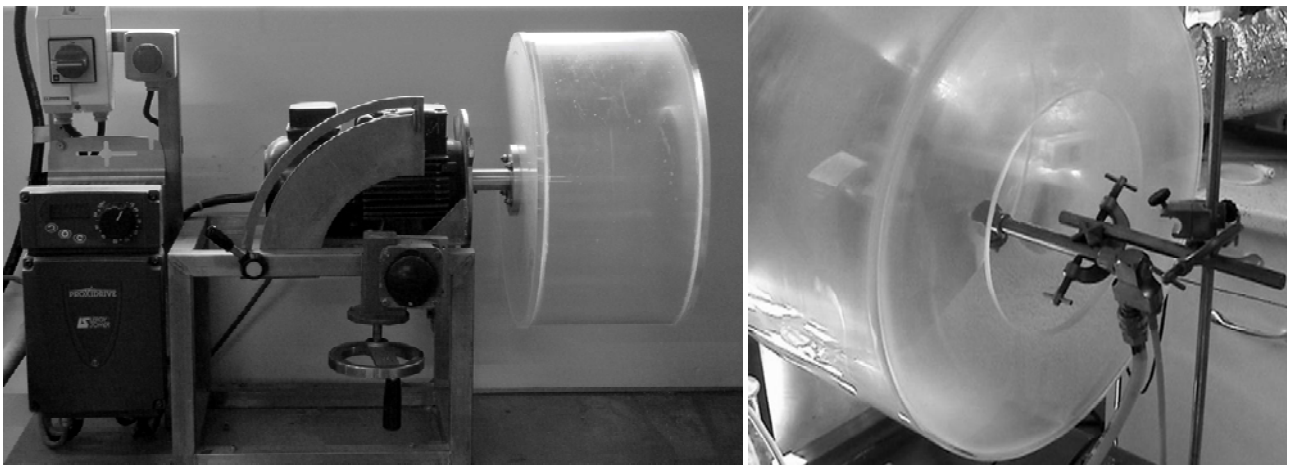

Fig. 1. ENITIAA prototype of Pan coater.

Optical microscopy: Particle shape and surface morphologies of coated particles were observed with a stereo-microscope (WILDMC3, Leica, Germany).

Scanning electron microscopy: The coated particles were also observed by a scanning electron microscope (SEM) (JSM-6400M, Jeol, Japan). Coated beads are broken and then sputter coated with gold for 30s. Whole samples and cross sections were mounted onto circular aluminum stub and analyzed. The aim of this analysis was to visualize the surface morphology and the film coating thickness and integrity.

Confocal laser scanning microscopy: A Bio-Rad Radiance 2000 Confocal Laser Scanning Microscope (Bio-Rad, UK), combined with a Nikon Eclipse TE300 inverted fluorescence microscope (Bio-Rad, UK) were used in order to check the quality of the coating.

The settings of the CLSM and the imaging window of the microcapsules were controlled by using the software Lasersharp 2000 version 5.2 (Bio-Rad, UK). The settings of the microscope were kept constant for all the measurements: laser power: 20% of maximum power; iris: 6.0; offset: 1.0; scan speed: 500 lines/second.

The chromophore compound used to be detected by CLSM was Rhodamine B and the amount of it charged in the plasticizer solution was 100mg per 400g of pellets.

Experiment for 6%,12% and 18% coating levels have been analyzed. Images of 100 coated beads were recorded under the CLSM. These images were then analyzed by using the ImageJ software. Data from ImageJ were transferred to Microsoft Excel and the coating thickness and quality parameters were calculated by the Depypere protocol [8].

3. RESULTS AND DISCUSSIONS

The process has been performed at the parameters previously described, and coating efficiency results of around 85% were obtained for some of polymers, as reported in Table 1.

Table 1. Results of dry coating process

Polymer	Mean diameter	Coating process efficiency	Coating aspect
Malto Dextrin	80µm	40 ± 10	Presents of aggregates
Starch octenyl succinate	50µm	50 ± 10	Presents of aggregates
Tapioca Dextrin	30µm	85 ± 5	Homogenous shell
Aluminium starch octenyl succinate	20µm	85 ± 10	Homogenous shell
Octenyl succinate dextrin of waxy maize	20µm	85 ± 7	Homogenous shell

3.1. Role of plasticizer

Two different kinds of plasticizers have been used in this dry coating process. The choice of materials as Triethyl Citrate and Glycerol has been justified by the description of these compounds in literature as good plasticizers for starch [9]. A plasticizer generally produces a lower softening temperature and a decrease in glass transition temperature (Tg) of polymer film.

In the dry coating method the continuous film formation is achieved by increasing the temperature during the curing step. Compared with the conventional method no water with plasticizing quality has to be evaporated because no volatile plasticizer like water is in use.

Results have shown possibilities to use both above-mentioned compounds and no occurrence of coalescence of polymer particles onto the pellets surface at room temperature.

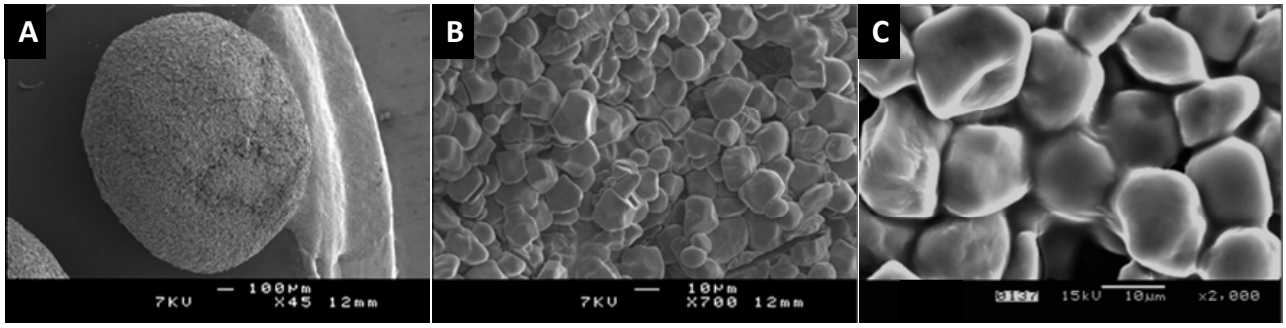

Fig.2. SEM image analysis of MCC particles coated with Octenyl succinate dextrin of waxy maize: entire pellet (A), pellet surface (B) and pellet surface enlargement after curing (C).

In this case, the plasticizer material behaves like a binding agent during the process and not as a plasticizer in its litteral meaning.

Scanning Electron Microscopy (SEM) has shown that polymer particles are uniformly compacted on the MCC pellets surface (Fig. 2A).

Coated beads with octenyl succinate dextrin of waxy maize show a beginning of coalescence formation of particles at room temperature (Fig.2B) and after a curing step at 50° for 45min, particle coalescence is marked and evident (Fig.2C).

3.2. Influence of particle shape and size.

A low coating process efficiency, due to aggregates presents onto the pellets surface, was recorded during experiments conducted with some of the polymer used.

This low process efficiency could be explained by the particle shape and size of the polymer. Polymer particles with a needle shape do not allow to get a layer formation caused by their incapability to stick onto pellets surface (Fig.3A). In parallel, during the process, particles with a spherical shape (Fig.4A) behave like a flowing agent and for this reason the particle motion can't be controled in the reactor, which makes uniformly coating of the particles an impossible task.

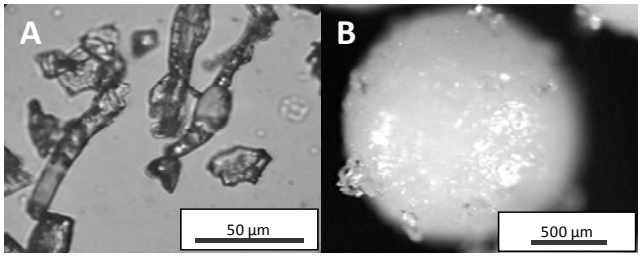

Fig. 3. Particles (A) and pellets (B) coated by Malto-Dextrin.

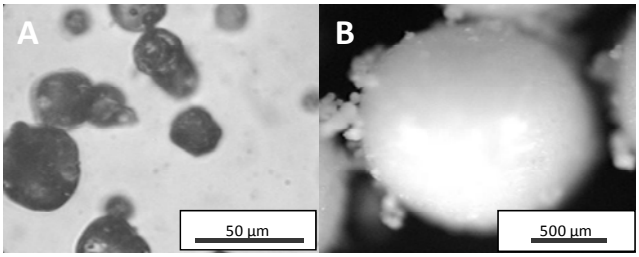

Fig. 4. Particles (A) and pellets (B) coated by Octenyl succinate starch.

Figures 3B and 4B show particles coated with MaltoDextrin and Starch octenyl succinate. Trials conducted with these polymers have shown the presence of polymers aggregates onto MCC pellets surface, and in particular in Fig. 3B, where the shiny pellets surface shows that the plasticizer sprayed coated the pellet's surface and only some polymer aggregates remains attached to it. Therefore it was not possible to use particles with these properties in order to obtain a coating layer.

With regard to particle size, results have shown that a coating process performed by a polymer with particles size more than 50µm has a low coating process effieciency. It could be explained because particles bigger than 50µm are not in close contact with the pellet surface for a time enough to obtain a layer formation. They remain in the reactor during the process but they don't take part in the coating process, remaining as discarded material.

Instead particles under 50µm (Fig. 5A and 6A) have show a good ability to form a coating shell with quite uniformity of thickness (Fig. 5B and 6B) onto the pellets surface.

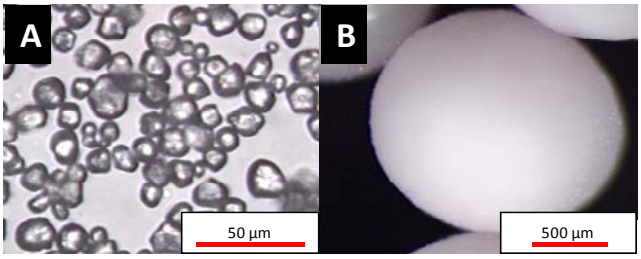

Fig. 5. Particles (A) and pellets coated by Tapioca-Dextrin (B)

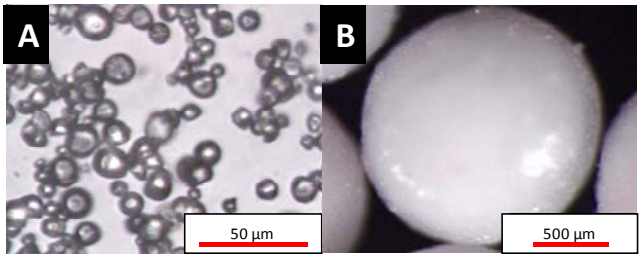

Fig. 6. Particles (A) and pellets coated by Aluminium octenyl succinate starch (B).

3.3. Coating quality analysis

A study has been done with Confocal Laser Scanning Microscopy (CLSM) in order to investigate the possibility to apply this kind of microscopy on dry coated particles and to measure the quality of the coating.

Rhodamine powder has been previously mixed with liquid plasticizer. The use of this mixing permitted to detect chromophore fluorescence by CLSM technique. The innovation about CLSM employment in the dry coating technique results on the one hand in the possibility to detect plasticizer matrix inside the coating layer, on the other hand we are able to measure coating thickness after image analysis.

CLSM was introduced as a new method to characterize particles coated by an unconventional process, like the dry coating technology. As supposed, a progressive increase of coating layer thickness together with an increase of coating level from 6% to 18% was found.

Table 2. Results of CLSM analysis obtained on 100 beads analyzed.

Coating Level	Coating thickness average (δ)	Heterogeneity (η) (st dev of coating distribution)	Coating quality (η / δ)
6%	18,59 µm	10.25	0,55
12%	22,19 µm	10,51	0,47
18%	24,87 µm	9,90	0,40

The results have also shown high values of standard deviation, that means a low homogeneity of coating. This needs however to be considered together with the high values of coating thickness measured.

A parameter of coating quality η/δ (heterogeneity/thickness average) has been considered in order to define a value of coating quality in a range scale from 0 to 1. This value, calculated at different coating levels, permits to quantify coating quality. As there is an increase of coating level, an increase of coating quality is observed (Fig.7).

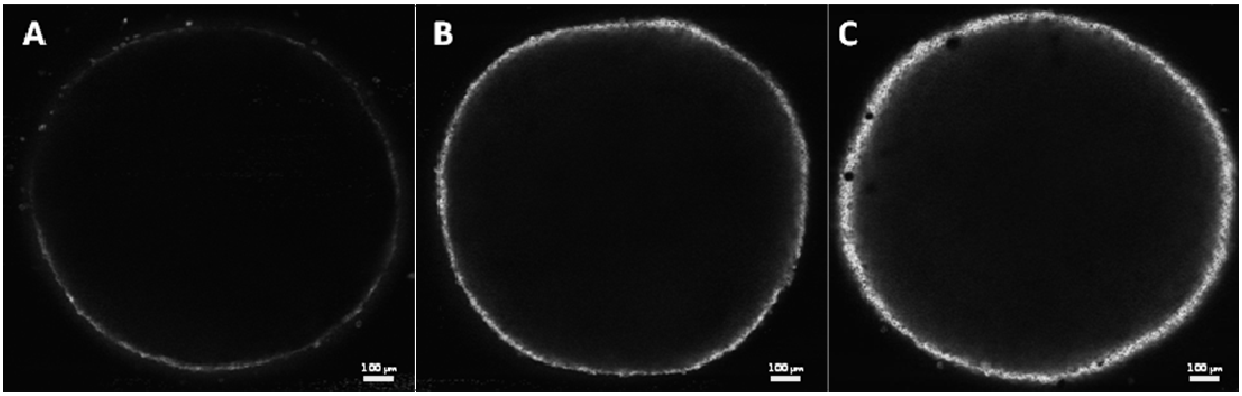

Fig.7. Epifluorescence CLSM images of pellets coated by Octenyl succinate dextrin of waxy maize at 6%(A), 12%(B) and 18%(C).

4. CONCLUSIONS

The results have shown the feasibility of a dry coating process in the Pan Coater device. The use of formulation with modified starches has shown a capability to produce coated particles with small losses of coating material at room temperature.
It is possible to obtain an uniform coating with polysaccharides particles of a size under 50µm and polygonal shape.
This coating process is a highly efficient process (a short processing time of 20-25min causing low energy consumption) compared to standard coating process.
We have shown the applicability of Confocal Laser Scanning Microscopy as a new characterization technique on dry coated particles. Results obtained by CLSM have shown, for each coating level, a real increase of coating thickness and as well of coating quality.
Further experiments are in progress to improve homogeneity of the coating shell and coating quality in order to propose this approach of polysaccharides coating for industrial employment.

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6. NOMENCLATURE

M_{cP} = coated pellets mass (g)
M_{uP} = uncoated pellets mass (g)
M_{Poly} = coating polymer mass (g)
M_{Plas} = plasticizer mass (g)
MCC = Micro crystalline cellulose
η = Heterogeneity
δ = Thickness average

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