Encapsulation of water sensitive products: effectiveness and assessment of fluid bed dry coating

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Abstract

Today, there is a real interest in the use of products containing some living cells or some other fragile substances in many industries, agriculture, chemical, pharmaceutical and food, because of their beneficial functional properties and effects on the environment and human health. These products are used or processed as dried substances to enhance their stability, viability and activity and they are generally encapsulated or attached to a support (tablet or coated particles) for these purposes. The problem is that with all traditional aqueous coating processes, these products can come in contact with water and can loose all their beneficial characteristics. A new method for encapsulating such material, which consists in coating directly the core material with a fine dry powder, is described here. A comparison with the classical aqueous coating system will show various advantages such as high coating yield and energy saving in addition to the non-wetting of the product. The resulting dried coated particles are very permeable and can be dissolved rapidly in water. The results also show some disadvantages such as the high hygroscopicity and the low strength of the coating film. These disadvantages, along with the water uptake during the process (2%) indicate that this dry coating system, which presents some real potential for industrial application, needs some improvements, especially the suppression or the reduction of water in the fluidising and atomizing air.
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1. Introduction

Today, more and more biologically active substances are used in various industries because of their beneficial functional properties and effects on the environment and human health. These products can be classified into three categories:

(1) Nutraceuticals are functional foods (Pascual, Hugas, Badiola, Monfort, & Garriga, 1999; Sanders, 1999) whose demand is growing because the consumers now spend less time cooking per day and they also demand safer, more hygienic and healthy foods (e.g., the

European market was estimated at (€) 1000 million in 2000) (Meesters, 2002).

(2) New proteins and enzymes are activated in the presence of water. Indeed their humidification can increase the activity of such enzymes, initiating some undesired reaction and the subsequent dehydration step reduces the activity of the protein (Potts, 1994).

(3) Coated seeds are more and more used in agriculture today, in order to reduce the quantity of pesticides and mineral or organic fertilisers for environment protection. These seeds are coated sometime with living inoculums to fix atmospheric nitrogen or phosphoric mineralization in the field, to assist in the uptake of mineral nutrients from the soil, etc. During the coating process, the final water content of the seed should not

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exceed about 10% to prevent fungal growth for example (Abdullah, 2000; Martinez et al., 1998).

It is evident that these products are very sensitive to water. The most important thing to do, for saving the positive effects of these functional products, is to keep a large quantity of active (bacteria, minerals or fats) components in the final ready-to-use products (granules, pellets or tablets). Most of the time, these products are protected by different aqueous coating techniques successfully but when the active components are too sensitive to moisture these methods are not suitable any more. Indeed, during the aqueous film coating process, the humidity in the coating chamber increases significantly and Clementi and Rossi (1984) demonstrated that the viability of dry-probiotics decreases rapidly. Dry coating is an alternative to these conventional methods that can allow maximum saving of the viability and activity of the active components by minimising the effect of atmospheric moisture on their shelf life.

Dry coating is not really a new technology (Obara, Maruyama, Nishiyama, & Kokubo, 1999). It had been applied in chemical, aeronautical, metallic (Alince & Lepoutre, 1983), wood and paper industries mostly for coating or recovering woods, metals or any desired surface by paints, varnishes, different polymers or precious metal to protect them against corrosion or to reinforce them. Its application to food area is quite recent and is still in its infancy.

Strictly, dry coating refers to techniques where the core materials are strongly surrounded by fine particles either by collision or by the use of non-aqueous binders. But dry coating for food ingredients covers all techniques that allow coating the core material without wetting with water. So defined, uses of non-aqueous solvents and hot melts are considered as dry coating techniques. Finally, there are four main approaches to dry coating, the principles of which are summarised in Fig. 1:

(1) The use of non-aqueous solvents in traditional coaters enhances the material efficiency of the coating process by increasing the solid content (from 4% to 20%) of the sprayed coating material while keeping low viscosity. The process can take place in all types of coating systems. The coating material is dissolved in a solvent, which is evaporated after spraying onto the core material (Fig. 1a). The main drawback of this approach is the emission of solvents to the atmosphere, the solvent residue in the final product and the explosion risk. The permittable emission rate for solvents, which is determined by the local authorities, is being more and more reduced by European regulations. Note that, even with the use of an expensive solvent recovery system, 5–10% of the solvent is not recovered.

(2) Hot melt coating consists of using some molten materials such as solid fats, waxes and some polymers as coating materials providing a shell with very good barrier properties against water vapour. During this process, which can take place in all types of fluid beds, the hot melted coating material is sprayed on the core material and solidified directly by cold air. The core material is then never in contact with water (Fig. 1a). This dry coating approach is known for its low cost and it presents many advantages: no solvent used, i.e. sprayed liquid = 100% coating agent, short processing time, no drying step required (Prasch, 1998). The main drawbacks of hot melt are its non-adaptation to heat sensitive (biological) products, poor flow properties, strength and perhaps an odour (due to oxidation) from the coated particles. In addition the final product is not immediately soluble in water at room temperature.

(3) Dry particle coating, as shown in Fig. 1b, consists in coating relatively large particle size (core material or host) with fine particles (guest) using mechano-chemical treatment with no wetting. This leads to coated particles that can dissolve quickly in water because of their high porosity. The technique requires new blending
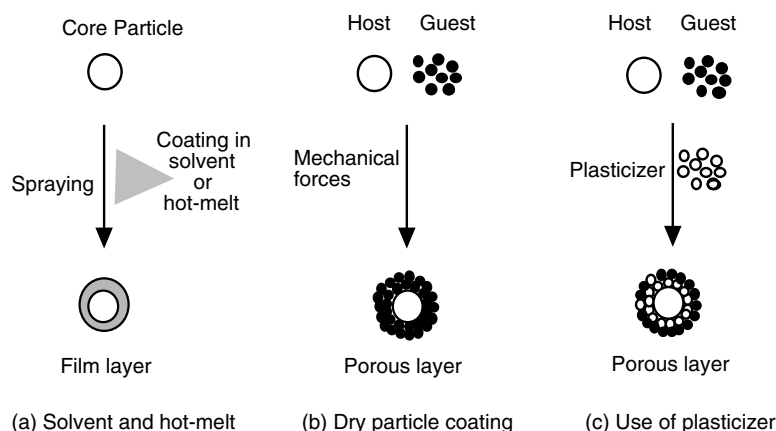

Fig. 1. Principles of different dry coating approaches.

machines (Alonso & Alguacil, 2001; Pfeffer, Dave, Wei, & Ramlakhan, 2001) and the strength of the bonding between the guest and the host particles is sometime so weak that a curing step is necessary to achieve strong bonding.

(4) Dry coating with plasticizer consists in fixing fine particles on the core using a non-aqueous binder or a plasticizer (Fig. 1c) instead of mechanical forces. This novel technique was developed by the Japanese company, Shin-Etsu (Obara et al., 1999; Shin-Etsu chemical co. Ltd., 1997). The technique was welcomed in the food and pharmaceutical industries because of obvious advantages: no deformation of the resulting coated particles and no investment in one of the new blending machines mentioned above as the process can take place in any conventional coating system providing a powder feeding unit.

Our research concentrated on this last coating technique, the objective being to compare the granules obtained by aqueous and dry coating systems. The formed coating shell was tested, for permeability, water content, solubility in water and mechanical resistance. Emphasis was placed on the optimisation of the operating parameters (flow rate of the plasticizer through the nozzle, air pressure for atomization and powder feed rate) and on different advantages of the dry coating system compared to the traditional aqueous coating system.

2. Materials and methods

2.1. Materials

White spherical beads of crystalline cellulose (IPS, Cellts), with a mean particle diameter of 835 μm and a density 828 kg/m^3, were used as core materials (host particles). Their initial water content (6%) was too high compared to the recommended 0.5% for sensitive products. So, the beads were dehydrated in a drying oven for 48 h at 100 °C and cooled after (using a desiccator) before coating.

For aqueous coating, a 3% aqueous solution of SEPI-FILM LP 010 (SEPIC, Paris, France) was used as a coating solution. SEPIFILM consists of hydroxypropyl methylcellulose, microcrystalline cellulose and stearic acid.

For dry coating, a combination of polymers was used: a fine coating powder as guest particles, also called AQOAT (SYNTAPHARM, Mülhein, Germany), which consist of hydroxypropyl methylcellulose acetate succinate and talc powder plus the liquid plasticizer (triethyl citrate, Sigma and acetylated monoglyceride) in the following proportion: 7 ml of plasticizer for 30 g of AQOAT. The particle size of the guest particles was not more than 10 μm.

Dyes were added to the aqueous solution and the plasticizer solution to colour the formed coating shell. This precaution is necessary for the dissolution test.

The classical lab-scale Wurster (a bottom-spray coater) UNIGLATT (Glatt, Binzen) was used for aqueous coating (Fig. 2, frame A). A fine powder-feeding device was adapted to this system for dry coating as specified in Fig. 2, frame B.

2.2. Experimental procedure

After the optimizing of the process parameters, crystalline cellulose beads were coated using the aqueous and dry coating technique. The two types of coating operation were carried out as described below. Those parameters are reported in the following descriptions.

Aqueous-coating with SEPIFILM LP 010:
500 g of dried cellulose core materials were first fluidized, then the 3% aqueous solution was sprayed at a rate of 5 g/min through the nozzle in the fluid bed chamber for coating. The atomization pressure was set to 1.5 bars. The temperature of the inlet and outlet air was respectively 60 °C and 42 °C. The experiment was run for 120 min. The temperature of the atmosphere around the fluid bed was 20 °C. A hydroclip probe (Rotronic, Switzerland) was used to record the relative humidity and the temperature of air in the fluid bed. Samples of granules in the fluid bed were collected for water content analysis using an infrared thermo-gravimetric humidimeter (Mettler Toledo, France).

Dry-coating system with AQOAT and plasticizer
The metal tube ($d = 15$ mm) of the powder feeding system was first positioned between the nozzle and the insert to allow homogeneous dispersion of the fine guest particles in the coating zone (Fig. 2, frame A and B). 500 g of dried cellulose core materials were then fluidized, followed by a simultaneous atomisation of the plasticizer at a rate of 1 ml/min and the dispersion of the guest particles at a rate of 2 g/min. in front of the nozzle in the fluid bed chamber for coating. The atomization pressure was set to 1.5 bars. The temperature of the inlet and outlet air was respectively 40 °C and 27 °C. The experiment was run for 30 min with no curing to keep the potential application to sensitive products. A curing step, which consists in turning the porous coating layer into a film layer by heating at 60 °C for about 30 min, was carried out in some few cases, especially for the study of its effect on dissolution properties of granules.

2.3. Particles analyses

2.3.1. Physical properties of different particles
The particles diameter was measured using a graduated microscope. The mean diameter was calculated from the diameter measurements of 50 beads.
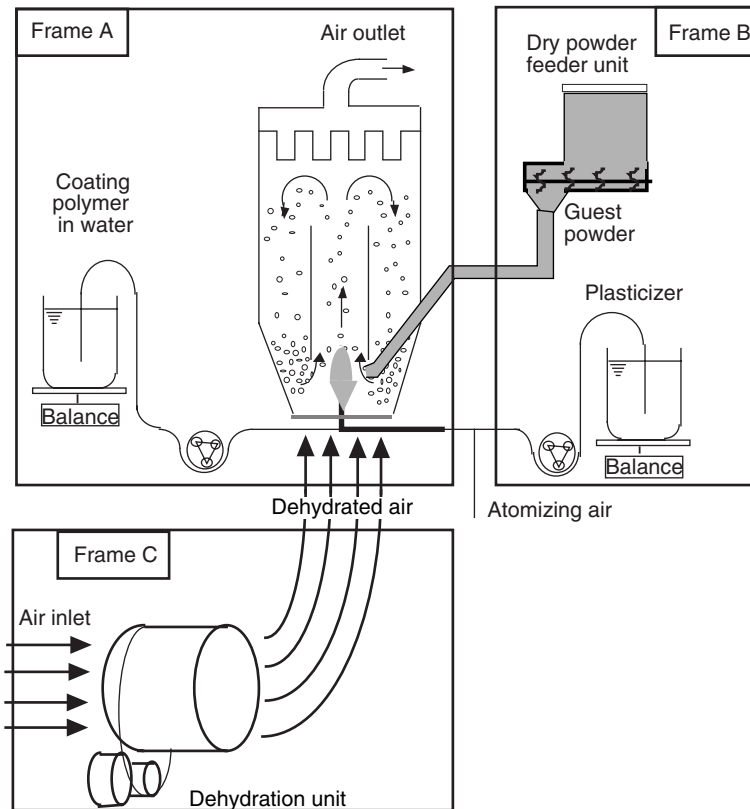
Fig. 2. A classical aqueous Wurster coaters (frame A) associated to: a dry feeder unit (frame B) a dehydration unit (frame C).

The thickness of the shell of granules was calculated as the half difference between the initial and the final diameter of the granules.

The water content of different particles was determined by the classical gravity method; Samples (approximately 10 g of particles) were maintained at 100 °C for 48 h in the oven and were weighted until constant weight.

2.3.2. Permeability of the granules

The hydration was measured using a desiccator. It consisted of a small box filled with $Mg(NO_3)_2$ and covered hermetically by a stopper. The granules (10 g approximately) were put in a cup, weighed and placed in the centre of the box. The granules were allowed to stand for 48 h and 168 h in the closed box in an oven at 25 °C. The final weight of the granules was measured for the calculation of the water uptake. At 25 °C, the $Mg(NO_3)_2$ provided a humidity of about 50% RH in the box.

2.3.3. Water sorption isotherms (25°C) of different particles

Approximately 0.4 g of particles were put into small dishes and dried. Then, each dishes was placed in a desiccator containing a saturated solution of salt that devel-

ops a given relative humidity in the desiccator. This latter was put in an oven at 25 °C for equilibrium. Various desiccators were used to create relative humidities from 11% to 96%. The dishes were weighed after 8 days (reasonable equilibrium time) and the water uptake was calculated to plot the water content versus the relative humidity, the so-called sorption isotherm curve.

2.3.4. Dissolution of the shell in water

For this experiment, 10 g of coloured granules was poured into 100 ml of water and the solution was mixed using a magnetic stirrer (800 rpm). The optical density of the solution was measured regularly and stopped when the coloured coating shell disappeared or when the white core beads appeared. This lapse of time was recorded as dissolution time.

2.3.5. Strength of the granules shell

There is no standard method to measure the strength of the shell around the beads. A simple method, using a rotary drum with an abrasive and perforated inner surface, was developed. It consists in rotating the drum containing 50 g of granules at a rotating speed of 75 rpm for 4 h. The rotating drum was weighted regularly to assess the quantity of material removed from the granules by abrasion.

3. Results and discussion

The results are presented here as a comparison of the aqueous coating and the dry coating systems. This approach may appear as inadequate for some parameters but it finds its justification in the fact that the aqueous solution (SEPIFILM) and the dry powder (AQOAT) are close in composition and were both designed to improve the stability of moisture sensitive ingredients.

3.1. The coating processes

During aqueous coating, the coating solution was collected on the inner cylinder wall as a dried and thin "paper" sheet, and this constituted a big loss at the end of the experiments. Despite different optimization strategies, this "paper" sheet could not be avoided during coating. At least its quantity could be reduced drastically to approximately 3% of the total coating material when the coating liquid was batch fed, i.e., the coating liquid was alternatively sprayed in the system for 5 min and stopped for five minutes allowing some drying. The final mean diameter of the coated granules was 856 μm, i.e. a shell thickness of about 10.5 μm.

It was observed during preliminary experiments of the dry coating that, above a coating flow rate of 2 g/min and a plasticizer flow rate of 1 ml/min, there was agglomeration of granules and a great loss of the guest particles which were dispersed in the fluid bed chamber before finally becoming stuck on the air filter of the fluid bed. This demonstrates the difficulty of running an experiment that is described as simple by (Shin-Etsu chemical co. Ltd., 1997) and the necessity of establishing the optimum operating conditions for each case. The final mean diameter of the coated granules was 870 μm, i.e. a thickness of about 17.5 μm and a coating shell, which consists of approximately a double layer of guest particles, assuming an ordered adhesion of the guest particles on the cellulose beads.

Dry coating is a quick process: Its processing time was a quarter of the aqueous coating time and led to a shell thickness that was about two times larger than the aqueous coating film. But its efficiency was significantly lower than that of conventional aqueous coating (96%). Indeed, despite the use of optimized parameters mentioned above, the efficiency of dry coating was 75%, the efficiency is calculated here as actual weight gain of coated samples divided by the theoretical weight gain. Note that, it is reported (Obara et al., 1999) that the efficiency can be increased to more than 95% in pilot-scale equipment.

3.2. Hydration during the coating processes

Table 1 presents the water content of the granules obtained by aqueous and dry coating. It appears that the

Table 1
Water uptake during the two coating processes

Coating time (min)	Aqueous coating		Dry coating	
	Solid coating material added (g)	Water content (%)	Solid coating material added (g)	Water content (%)
5			10	0.5
10			20	1
20	3	4	40	2
30	4.5	4	60	2
40	6	4		
60	9	3		
80	12	3		
100	15	4		
120	18	4		

granules from aqueous coating were always at 4% water content, while the average final water content of the granules from dry coating was 2%. This means that granules absorb water during coating under the process conditions in the fluid bed chamber. This can be explained by considering the variation in relative humidity and the water content during the aqueous coating process (Fig. 3). Indeed it appears that during the initial fluidisation step (no liquid spraying), the cellulose beads absorb about 2% water that corresponds to the amount of water found in the final granules after dry coating. As the spraying of the coating liquid starts, there is an increasing of RH and water content, due to high input of water, that levels at about 40% and 6% respectively after steady state. When the spraying of the coating liquids stops, the granules are submitted to a drying process that reduces their water content to 4% which corresponds to the amount of water found in the final granules after aqueous coating. To summarise, the main sources of water uptake in the fluid bed coating process are water from the coating solution (specifically for aqueous coating), and humidity of the air.
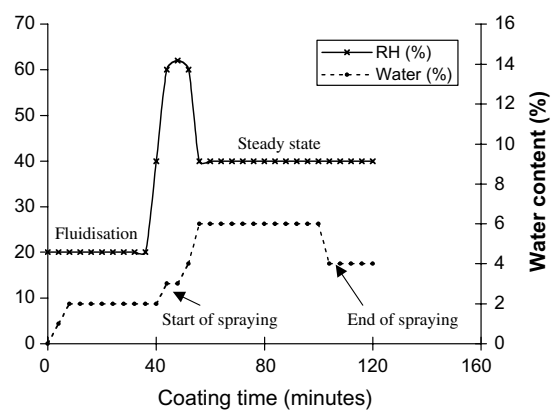
Fig. 3. Air relative humidity and granules water content during aqueous coating.

During dry coating, the water uptake can be suppressed, but this could not be done with the present dry coating system because the initial humidity of the fluidising air could not be controlled. This result has promoted one of the main perspectives of our actual research work: The monitoring of the fluidising and atomisation air (using a dehydrating unit as shown on Fig. 2, frame C) for an efficient coating of water sensitive particles.

3.3. Permeability of the shell (hydration of granules during storage)

Different methods exist for measuring the permeability of water vapour trough a membrane. The principle of these methods is to determine the quantity of water, which diffuses through the film or the membrane separating the humid space from the dried space. This principle was not applied here because large films of coating materials could not be prepared, that is why it was decided to rather measure the hydration of granules during storage in a relatively dry air.

The measurement of the final moisture contents after storage showed that the cellulose core beads without membrane and the granules absorb the same ratio of water (∼6%) after 48 h (Table 2). But, after 168 h, this ratio increases to about 8% for beads without a membrane and to 6% for aqueous and dry coated granules. Now, if considering the fact that the granule consists mainly of the core material (88% and 92 % V/V respectively for aqueous and dry coated granules), it can be said that aqueous and dry coatings could protect the cellulose core against water vapour, but not sufficiently because the difference of water content between cellulose beads and the coated granules was about 2%. This protection may be improved by increasing the plasticizer concentration as demonstrated by Park and Chinnan (1995), who found that the water vapour barrier properties of cellulose films increase as the concentration of plastisizer (Myvacet 7-00 TM) increases, while investigating the gas and water vapour barrier properties of edible films.

Finally, the protections by both aqueous and dry coating are similar and are not sufficient. The same remarks can be made while comparing the water sorption isotherms of the uncoated beads with the aqueous and dry coated granules (Fig. 4). So, the only way to maintain the advantage brought by dry coating (low
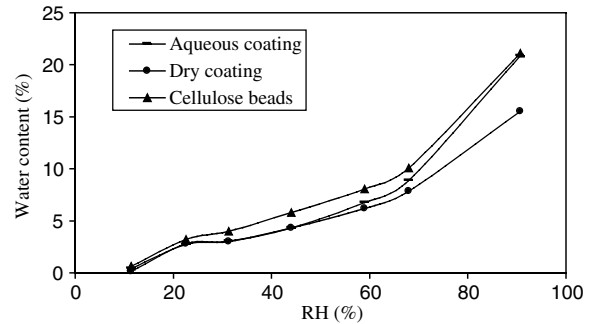

Fig. 4. Water sorption isotherms of cellulose beads and coated granules (25 °C).

hydration during the coating process) is to provide an adequate storage. The relatively high water content of coated particles and their hydration during the dry coating process and storage are future challenges to be overcome in order to apply this technology to water sensitive products.

3.4. Dissolution of the coating shell in water

The time required to disintegrate the shell of aqueous coated granules was about 120 s. This time was only 40 s for the dry coated granules (Fig. 5). This difference, at first glance, seems illogic because the thickness of the shell formed by dry coating (17 μm) is bigger than the thickness of the aqueous coating shell (10.5 μm). In fact, the behaviour of the granules shell in the presence of water depends on its structure rather to its thickness and in this case the structure of the thick shell formed by dry coating (arrangement of a double layer of fine AQOAT powder) is more favourable to hydration than the fine aqueous coating film. Changing the structure of the AQOAT shell will modify the dissolving time. A curing step, for example after dry coating, increases the dissolving time in water to over 10 min (Fig. 5). Curing normally transforms the deposit of fine solid

Table 2
Water uptake of cellulose beads and granules during storage

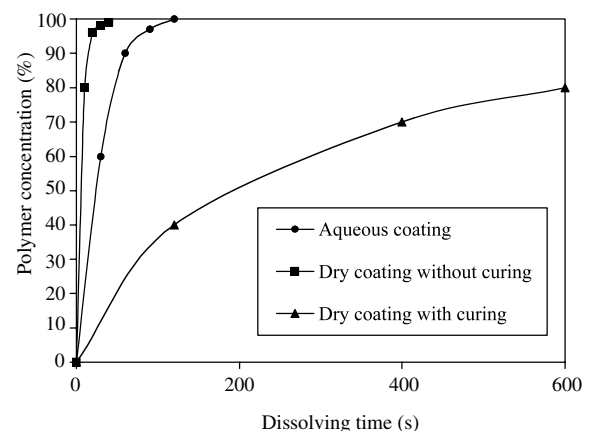| Storage at 50% RH	Cellulose beads	Granules (aqueous coating)	Granules (dry coating)
48 h	6%	6%	6%
168 h	8%	6%	6%

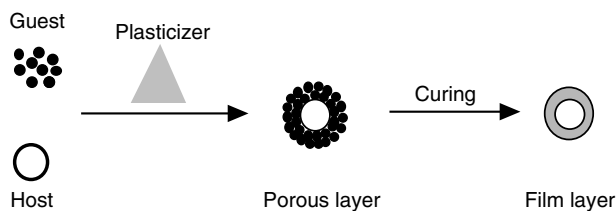Fig. 5. Solubility curves of different shell in water.

Fig. 6. Film formation after the curing step.

particles around the core into a film, as shown in Fig. 6, and therefore reduces the permeability of the shell to water.

3.5. Strength of the granules shell

Fig. 7 presents the granules weight versus time after their abrasion in the rotary drum. It appears that the dry coated granules are more fragile than aqueous coated granules. Once again, the structure of the shell of dry coated granules is involved here. Also note that, curing, by reinforcing its structure, can improve the strength of this shell. Theoretically, the sandpaper covering the inner surface of the drum should rasp the surface of the granules continuously but, as it can be seen on Fig. 7, the weight loss stops after 2 h in both cases. Two hypotheses can explain this situation: first, the shell of coated granules, which is progressively tightly packed after many tumbling in the drum, finally acquires a strength sufficient to resist the abrasion in the system. In parallel, the rough patches on the surface of the sandpaper are filled progressively, leading to a smooth surface of the sandpaper, which is not able to rasp the granules any more. Finally, is the present method suitable for testing the strength of the granules shell regarding their resistance during wall friction in various processes? This question, among other things, expresses clearly the problem of standardisation of characterisation methods in powder technology.
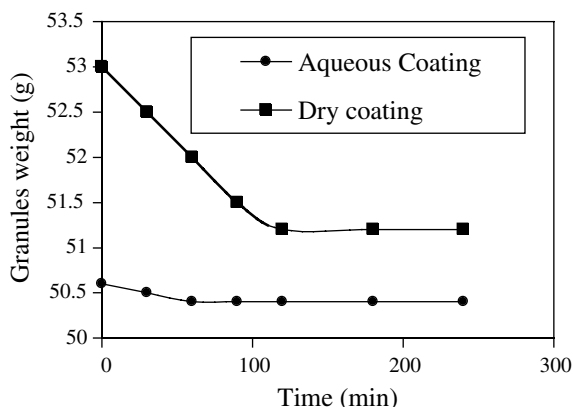
4. Conclusion

Dry coating, using a non-aqueous plasticizer, is the technique that looks promising, from all points of view, for coating food ingredients (time, energy savings and high productivity). This technique has a low moisture level compared with aqueous coating systems. However, quite a small level of water was detected in the granules (2%), and this is not acceptable for applications to some sensitive products such as probiotics. That is why further investigations are in process to design an air-dry system in order to improve the processing conditions (e.g. dehydration of the fluidising and atomisation air), the target being to reach very low relative humidity in the fluid bed chamber (less than 5%) in order to achieve low final water content of the granules for a long term storage.

Regarding the properties of the granules, it appears that there is a need for a powerful method that will allow accurate measurement of the percentage of water that can cross a given film on a coated particle. Emphasis must be placed on the formulation aspect to find the suitable combination and composition of plasticizers and guest particles that can fulfil the two opposite objectives (fast solubility in water and barrier for water vapour). Lastly, in addition to the functional properties of the granules for which testing is required to check the success of the coating process, the strength of the coated granules must be taken into account when dealing with dry coating. Outstanding research works have been published on this topic by (Schubert, 1974; Schubert, Herrmann, & Rumf, 1974), analysing the strength of agglomerates and presenting different testing method, but the selected method must adequately report the binding strength of the guest particles to the host particles surface. For example, an adapted abrasion test was developed actually in our laboratory for this purpose, which is designed in such a way that the mechanisms of constraint during the test correspond to what coated particles can encounter during their handling and processing.

Fig. 7. Weight loss of the granule during abrasion test.

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