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Assessment of coating quality by use of dissolution kinetics

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ABSTRACT

Fluid bed coating of powder is widely applied in the industry. Analysis of the production batch in terms of coating thickness and its distribution within the population cannot be performed easily. Microscopic analysis to accurately measure the shell thickness of a particle lacks the ability to give statistical information of the population within a reasonable amount of time. In this work, a novel method based on measuring the effect of the coating and solving the involved inverse problem is proposed as a fast way to measure the shell thickness distribution in the sample. The method was tested with sodium chloride particles coated with varying amounts of maltodextrin. It could be shown that coating thickness distributions between 0.2 and 20 μm can be measured with significant differences between samples.

1. Introduction

Encapsulation of drugs and ingredients is widely applied in the pharmaceutical and food industry in order to provide additional functionality (controlled or delayed release), protect ingredients from the environment (oxygen, other ingredients) or to alter surface properties (flowability, colour) [1].

In general, encapsulates can be divided into the reservoir and the matrix type. Whereas in the matrix type capsules, the active ingredient is dispersed more or less uniformly in the encapsulation agent, the reservoir type consists of an active core, the reservoir, and a shell around it [2]. The article focuses in the following on the reservoir type or shell coating encapsulates.

The morphological requirements on these coatings depend on the application. An effective taste masking needs a complete layer of coating with a certain minimum thickness, whereas a coating for a controlled release application needs a layer with a well defined thickness and/or porosity. Therefore different measures of quality can be defined for coated particles — a non-comprehensive list is given below.

- mean coating thickness
- distribution of thickness on a single particle
- distribution of thickness over the whole population
- porous or non-porous
- degree of surface coverage

Some of those parameters can be assessed with ease. For instance the deposited mass of coating material can be used to determine the mean theoretical coating thickness s_{th} using the following equation.

$$s_{th} = \frac{d}{2} \cdot \left[\left(1 + \frac{\rho_{core} \cdot m_{coating}}{\rho_{coating} \cdot m_{core}} \right)^{1/3} - 1 \right] \quad (1)$$

Here it is implied that a perfect sphere of core material with mass m_{core} and density ρ_{core} is covered with a homogeneous layer of coat with mass $m_{coating}$ and density $\rho_{coating}$. The diameter of the core material d is a mean particle diameter representing the population of the particles. Accounting for the fact, that the equation basically calculates the thickness from the known volumes of the core and coating, the mean diameter used should be the volume weighed mean diameter $\overline{d}_{4,3}$.

Other parameters are harder to assess. For instance the porosity of the shell could be measured by means of a diffusion test. Optical methods like the confocal laser scanning microscopy or micro-computed X-ray tomography are capable of producing optical slices through the particles. The thickness as well as the porosity of the shell can then be measured by image analysis techniques, as several authors reported previously [3,4].

However, these methods are rather time consuming, and especially the microscopic methods are only capable to give information about single particles. Measuring enough particles to obtain statistical information about the population like the distribution of the shell thickness within the powder batch would take an unreasonable amount of time.

This article proposes a method to determine the shell thickness distribution based on the measurement of the effect of the coating, in this case the delayed dissolution of the core, accompanied by the solution of

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the inverse problem incorporated in the interpretation of the obtained data.

The method described in this investigation was tailored for the analysis of shell coatings produced using fluidised bed coating. Encapsulates of this type could also be formed by methods like electrostatic atomisation which can specifically form porous coatings [5], coacervation, co-extrusion or by preparation of emulsions with multilayers [2].

The studied size range was core particles with a diameter of about 400 µm and a thin coating layer of up to 10 µm thickness.

2. Theoretical considerations and description of the method

To address the complexity of the problem, the method proposed is based on four assumptions:

1 the population consists only of perfectly coated particles following Eq. (1), porosities within the coating layer are neglected, since they are not expected in the used model system
2 the dissolution curve of a perfectly coated particle is the same as for an uncoated particle, except for a time shift τ, which is the time needed to dissolve the shell
3 the dissolution velocity of the shell is constant, so $\tau \propto s$ and
4 the dissolution curve of the population is the sum of the dissolution curves of all thickness fractions.

The population of coated particles consists of fractions with varying shell thickness each having a different value for the time shift τ. This results in a time shift distribution which can be expressed as a probability density function $x(t)$ in s^{-1}. The dissolution curve $c(t)$ for the coated material is then given by the convolution (indicated by the convolution operator $*$) of the dissolution curve $c_0(t)$ of the uncoated material with $x(t)$:

$$c(t) = c_0(t) * x(t). \tag{2}$$

This can also be written as the convolution integral:

$$c(t) = \int_0^t x(\tau) \cdot c_0(t-\tau) d\tau. \tag{3}$$

The time shift distribution can thus be found by deconvolution. The dissolution curves are measured in discrete time intervals,

$$\Delta t = \frac{t_{max}}{n}, n \in \mathbb{N} \tag{4}$$

which leads to discretised time points:

$$t_i = \tau_i = i \cdot \Delta t \quad , i = 0, 1, \ldots, n-1, n. \tag{5}$$

Thus the probability density function $x(t)$ is discretised as

$$x_i = x \cdot \Delta t \tag{6}$$

which leads to the discretised form of Eq. (3):

$$c(t) = \sum_{i=0}^{n} x_i \cdot c_0(t-\tau_i). \tag{7}$$

The above equation implies the following system of linear equations which can be solved for all x_i.

$$\begin{pmatrix} c(t_0) \\ c(t_1) \\ \vdots \\ c(t_n) \end{pmatrix} = \begin{pmatrix} c_0(t_0-\tau_0) & \cdots & c_0(t_0-\tau_n) \\ c_0(t_1-\tau_0) & \cdots & c_0(t_1-t_n) \\ \vdots & \ddots & \vdots \\ c_0(t_n-\tau_0) & \cdots & c_0(t_n-\tau_n) \end{pmatrix} \cdot \begin{pmatrix} x_0 \\ x_1 \\ \vdots \\ x_n \end{pmatrix} \tag{8}$$

Since the concentration at time t_0 is $c_0(0) = c(0) = 0$ the first row in the system above reduces to $0 = 0$. Therefore the system lacks one equation to be fully solvable. To account for this problem, the additional condition

$$\sum_{i=0}^{n} x_i = 1 \tag{9}$$

is introduced, which gives the missing equation. This condition makes sense, because x represents the mass fractions of coated material with different τ. The final form of the linear system, with the first row changed to the new normalising condition, then reads as follows:

$$\begin{pmatrix} 1 \\ c(t_1) \\ \vdots \\ c(t_n) \end{pmatrix} = \begin{pmatrix} 1 & \cdots & 1 \\ c_0(t_1-\tau_0) & \cdots & c_0(t_1-t_n) \\ \vdots & \ddots & \vdots \\ c_0(t_n-\tau_0) & \cdots & c_0(t_n-\tau_n) \end{pmatrix} \cdot \begin{pmatrix} x_0 \\ x_1 \\ \vdots \\ x_n \end{pmatrix}. \tag{10}$$

Due to numerical instabilities of the system and the reasonable condition that all x_i should be either positive or zero, a non-negative least squares smoothing is used to solve the linear system [6].

As already mentioned above, the solution of the linear system gives a time shift distribution. In order to obtain a thickness distribution, the x-axis has to be transformed from a time-axis into a thickness-axis. The condition for that is point three in the list above. The dissolution velocity v_d is found by taking the mass balance into account. The total mass of coating deposited on the surface of the particles is divided between all time-delay fractions under the assumption of a constant dissolution velocity.

3. Materials and methods

3.1. Materials

Table salt from the local grocery store (Gut & Günstig-brand, EDEKA AG & Co. KG, Germany) was sieved to a fraction between 355 and 450 µm and used as core material during the coating operation. A solution of 20 % w/w maltodextrin with 21 dextrose equivalents (MD21, Roquette Frères, France) and 0.2 % w/w Ponceau 4R (Lay Gewürze OHG, Germany) in purified water was prepared and used as a coating agent. All materials used were of food grade quality.

3.2. Software

Unless noted otherwise, all data operations were performed using Matlab v. R2014b (The MathWorks, Inc., USA). Some of the image processing steps were performed using ImageJ (v. 1.49 g, [7]). Data logging was performed using LabView (National Instruments Corporation, USA).

3.3. Coating operation

The coating operation was performed in a WS-CT-L top-spray fluidized bed dryer (Allgaier Process Technology GmbH, Germany) equipped with a model 970 two-fluid nozzle (Düsen-Schlick GmbH, Germany) with a nozzle orifice diameter of 0.5 mm. The atomizing air pressure was set to 1 bar. The air distribution plate had a diameter of 100 mm.

1200 g of table salt was loaded to the device and fluidized at a volumetric air flow rate of 85 $m^3 h^{-1}$. The inlet air temperature was maintained at 60 °C. After a bed temperature of 40 °C was reached, the coating agent was sprayed at a spray rate of 7.5 g min^{-1}. The process was interrupted four times to remove 100 g of sample after 300, 275, 250 and 225 g of coating agent was sprayed. The material removed was not replaced, which could have had an impact on the process efficiency. This resulted in a theoretical loading of dry coating material of 5, 10, 15 and 20 % w/w on the core particles, without considering any losses due to overspray and/or attrition.