Functional encapsulation of small particles
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Chapter 8

TAILORING THE SIZE AND THE SPATIAL DISTRIBUTION OF PORES IN THE COATING FILMS MADE IN A FLUIDIZED BED COATER

Abstract

Up to now, the possibilities for quantification of coating morphologies are limited, which leads to the difficulties in assuring the coating performance and also little understanding on the film formation mechanism in a fluidized bed coating process. In this paper, the size and the spatial distributions of pores were quantified using a dedicated image analysis method and their evolution during the coating process was investigated. Moreover, the influence of various process settings, i.e. nozzle position, inlet gas flow rate and atomization pressure on the pore properties in the films were studied. The results showed that the deposition of moist droplets on the coating polymer causes the re-dissolution of the polymer that induces polymer flow and leads to the densification of the film. For this reason, pore size reduces in time and the pores in the outer part of the coating films were shown to be the first that disappeared upon layering. To facilitate this mechanism, it is important to have the droplets wet enough when they reach the particles, i.e. via immersing the nozzle in the bed (bottom-spray system). Moreover, it is also important to provide sufficient coating time with respect to the number of layering cycles to achieve optimum reduction of pores in the coating films. The latter aspect can also be tailored via adjusting the inlet gas flow rate as well as the atomization pressure.
8.1. Introduction

Control of the morphologies of coatings applied on small particles, specifically the thickness distribution and the porosity of the coating layer applied in a fluidized bed coating process are indispensable to achieve a certain barrier or transport properties (2, 3). In practice, the coating thickness is steered by determining the end of the fluidized bed coating process from the final amount of the coating sprayed during this process. This method will of course only lead to the desired average coating thickness. However, the coating thickness distribution is usually not uniform. Moreover, the presence of pores is almost inevitable in the coating films made using aqueous coating systems, due to high viscosity and relatively slow drying of droplets (4). This also explains the differences found between the actual coating thicknesses and those estimated from the amount of coating sprayed in our previous work (161). Keeping the coating porosity and pore size at minimum levels is obviously not only important to achieve a high barrier film but also to make the coating thickness easier to control. In spite of its importance, coating layer porous structures are still difficult to control in real-time process.

The control of the coating porous structure should include the control of both the total porosity and the distribution of the pores in the coating layer. Correlations between the total porosity and the transport properties, e.g. diffusion coefficient have often been reported in the literature (e.g. 5, 12, 135-136). Moreover, the variation of the pore locations in the coating films may lead to different transport mechanisms, e.g. the presence of pores close to the surface of the coating layer could facilitate pore condensation that leads to the increase of gas sorption to the films (189). The spatial distribution of pores in the coating layer has however not been well investigated.

This motivates this study to look at the way the coating layer is built up in a fluidized bed coating process. The formation of coating layer starts with the deposition of droplets on particle surface, which is influenced by the conditions of the droplet spraying entailing e.g. the size of droplets and the location of nozzle. Moreover, the coating time determines the progress of the layering cycles by droplets and therefore the coating quality, as revealed in our preliminary investigation illustrated in Figure 8-1. Quantitative image analysis is applied to measure the spatial distribution of pores in the coating films, next to the total porosity and the pore size distribution. In this way, the mechanism of the porosity evolution in time can be studied more comprehensively.
8.2. Materials and Methods

8.2.1. Materials

Microcrystalline cellulose/MCC (Avicel PH102, FMC BioPolymer), supplied by Internatio, (Zutphen, the Netherlands) was used as pellet excipient. Pellets were made using high shear granulation process described in Laksmana et al. (161). Hydroxy-propyl methylcellulose/HPMC (Methocel E5 LV USP/EP premium grade, Dow) supplied by Colorcon (Dartford Kent, UK) was used as coating polymer material. Carmoisine (E122, Pomona BV, Hedel, the Netherlands) was added as pigment in the coating.

8.2.2. Experimental Methods

8.2.2.1. Fluidized Bed Coating

The pellets with size fraction of 800-1000 micron were coated in a fluidized bed coater (Mycrolab, Oystar Hüttlin, Schopfheim, Germany). Samples (about 2-3 g) were taken at different coating time during process. The size of droplets sprayed was varied by changing the atomization pressures or the spraying rate. Inlet gas flow rate was also varied to study the influence of the number of layering cycles on the pore structure of the films. The coating solution was fed either from the bottom or from the top of the fluidized bed column. The process conditions used for present experiments are listed in Table 8-1. The drying
temperature was kept constant for all experiments at 70°C. The coating process was performed until about 20% weight ratio of coating to core was sprayed.

### Table 8-1. Experiment conditions used for fluidized bed coating process performed in this study

<table>
<thead>
<tr>
<th>Test</th>
<th>Nozzle location</th>
<th>$X_{\text{HPMC}}$ (%w/w)</th>
<th>Inlet gas flow rate (m3/h)</th>
<th>Atomization pressure (mbar)</th>
<th>Spraying rate (g/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BS1</td>
<td>Bottom-spray</td>
<td>5</td>
<td>25</td>
<td>1.5</td>
<td>4.8</td>
</tr>
<tr>
<td>BS2</td>
<td></td>
<td>5</td>
<td>25</td>
<td>0.5</td>
<td>4.8</td>
</tr>
<tr>
<td>BS3</td>
<td></td>
<td>5</td>
<td>25</td>
<td>1.5</td>
<td>2.4</td>
</tr>
<tr>
<td>BS4</td>
<td></td>
<td>5</td>
<td>25</td>
<td>1</td>
<td>2.4</td>
</tr>
<tr>
<td>BS5</td>
<td></td>
<td>5</td>
<td>25</td>
<td>0.5</td>
<td>2.4</td>
</tr>
<tr>
<td>BS6</td>
<td></td>
<td>5</td>
<td>20</td>
<td>1.5</td>
<td>2.4</td>
</tr>
<tr>
<td>BS7</td>
<td></td>
<td>5</td>
<td>25</td>
<td>1.5</td>
<td>1.2</td>
</tr>
<tr>
<td>BS8</td>
<td></td>
<td>10</td>
<td>25</td>
<td>1.5</td>
<td>2.4</td>
</tr>
<tr>
<td>TS1</td>
<td>Top-spray</td>
<td>5</td>
<td>25</td>
<td>1.5</td>
<td>4.8</td>
</tr>
<tr>
<td>TS2</td>
<td></td>
<td>5</td>
<td>25</td>
<td>1.5</td>
<td>2.4</td>
</tr>
<tr>
<td>TS3</td>
<td></td>
<td>5</td>
<td>20</td>
<td>1.5</td>
<td>2.4</td>
</tr>
<tr>
<td>TSBS1</td>
<td>Top-spray followed</td>
<td>5</td>
<td>25</td>
<td>1.5</td>
<td>4.8</td>
</tr>
</tbody>
</table>

### 8.2.2.2. Characterization of Coating Qualities

The characterization of coating qualities involves the determination of coating thickness distribution, porosity and pore size distribution, which were identified as important quality attributes of the coating films. Their determinations were based on a quantitative image analysis method, which is described in Laksmana et al. (161). The spatial distribution of pores in the coating films was determined using additional calculation steps, which are illustrated in Figure 8-2.

Figure 8-2(A) shows a typical confocal scanning laser microscopy (CSLM) image acquired for the pore structure analysis. Using a binarization procedure described in Laksmana et al (161), a binary image as in Figure 8-2 (B) was derived. The next step was to determine the inside and outside boundaries of the coating layer. The inside boundaries are the boundaries between the surface of the core particle and the coating layer, while the outside boundaries are the ones at the most outer part of the coating layer. In Figure 8-2(B), the inside and outside boundaries are presented with blue and red markers, respectively. A further sectioning of the coating layer was made to only include the part of the coating which both inside and outside boundaries are captured in the image. The selected section is shown in Figure 8-2(C) from which the spatial distribution of pores was further determined. Pores
are constituted of one to several pixels, which in this figure are marked with green colors. The Euclidean distances between a pore pixel and every point at the inside boundaries were calculated. The shortest distance was then taken as the position of the pore pixel to the inside boundaries i.e. the core surface. This calculation was performed for all the pore pixels, using image processing tools from Matlab® R2007A. Figure 8-2(D) illustrates the determined position of all pore pixels to the core surface given as red lines, which connect each pore pixel to the closest inside boundary (marked with blue color). In this way, a range of distances between the pores and the core surface and the number of pores that have such a distance can be obtained. In this figure, the final spatial distribution of pores is described as the (area) distribution of the porosity fraction at different fraction of the coating thickness, where “0” locates the fraction of pores at the core surface while “1” locates the one at the most outer part of the coating layer (the maximum thickness).

![Figure 8-2. Calculation steps used to determine the spatial distribution of pores in the coating layer (taken from samples of experiment BS1 after 19 minutes of coating, explanation see text).](image)

The pore structure analysis was performed on films produced at various process settings and process times. Unless mentioned, the presented analysis results were taken from
the data of films taken at the end of coating process, *i.e.* when coating polymer on particles was about 20% w/w.

### 8.3 Results and Discussion

#### 8.3.1 The reduction of the total porosity during coating process

As illustrated in Figure 8-1, the porosity in the coating film was found to initially decrease in time, leading to different porosities at different process settings. Here examples are taken from coating processes performed using a bottom versus a top-spray nozzle at constant spraying rate (4.8 g/min), inlet air temperature (70°C), and atomization pressure (1.5 bar). These two types of process lead to significant differences in the final porosity, *i.e.* 3% for bottom-spray versus 6.7% for top-spray system after 20% by weight coating polymer has been sprayed. These differences are correlated to the differences in the traveling distance for droplets before they reach the particles and therefore the drying and the deposition of the sprayed droplets, which were described in our previous study (190). In the top-spray system used, the nozzle was located about 4 cm above the bed. So, droplets could partially or completely be dried or even elutriated from the bed before they reach particles. As a result, the bed particles was less moist than those in the bottom-spray coating process using similar spraying and gas flow rate. This situation is confirmed in Figure 8-3, where the bed temperature was found higher *i.e.* the bed humidity was lower in the top-spray than in the bottom-spray coating process. Moreover, the material loss in the top-spray coating process was found to be much higher (~11%) compared to that in the bottom spray coating process (~4%). The lower amount of droplets reaching the particles and the higher viscosity of droplet aerosols when they reach the particles would lead to poorer particle coverage, which explains the high final porosity obtained from the top-spray coating process.

The reduction of the total porosity with coating time suggests a certain layering mechanism in a fluidized bed coating process that alters the structure of the coating layer in time. There are three mechanisms that can be considered possible in causing reduction in the coating porosity: (i) formation of a much denser layer on top of the previously formed coating layer that makes the average porosity of film become lower; (ii) pore-filling by polymer deposition in the pores; and (iii) rewetting of the coating matrix that induces polymer flow and densifies the coating matrix. In all cases, the coating layer may become more porous close to the particle core and denser at the outside of the layer. In case 1, the reduction of porosity can occur without any alteration of the structure of the coating layer.
beneath. Through layering sequence, it is possible that a denser layer is formed on top of the precursor coating layer, simply just because the adhesion between the droplets and the surface is improved. On contrary, when the reduction of the total porosity is via scenario 2 or 3, the alteration in the pre-existing coating layer is expected, which should be confirmed with a significant reduction of the pore size. Taking into account of these aspects, the plausibility of these three scenarios was tested and become the topic of the next section.

![Figure 8-3. Differences in the bed and outlet temperatures in the bottom and the top-spray coating processes (same experiments as in Fig. 8-1).](image)

### 8.3.2. The mechanisms of pore reduction

The pore size distribution analysis revealed that the pore size decreases in time for both bottom and top-spray coating processes, as shown in Figure 8-4. The degree of the reduction of the pore size in the top-spray, however, differs from that in the bottom-spray coating process. In the top-spray coating process, the pore size appears to only slightly decrease in time. This implies that the reduction of the total coating porosity in time in the top-spray coating system is unlikely via the reduction of the pore size and instead more likely via the subsequent layering by a much denser layer on top of the porous pre-formed film (scenario 1).

In the bottom-spray coating process, the pore size, in particular the larger ones ($d_{pore,90}$) was found to steadily decrease in time. Accordingly, the span of the pore size distribution, i.e. the difference between the $d_{pore,90}$ and the $d_{pore,10}$ becomes smaller in time as pointed in Figure
8-4. Unlike in the top-spray coating system, the scenario 1 was unlikely the cause of the reduction of total porosity in the bottom-spray coating process, as the bigger pores did reduce in time. This was also confirmed by the visual evaluation of coating structure obtained at different coating time (see the inserted CSLM images on the right-side in Figure 8-5). It can be seen that pores disappear with the increase of coating time, starting from the outer part of the coating (compare the CSLM image of particles taken after 19 and 76 minutes of coating). This preferential direction of pore reduction is expected considering the rewetting direction of the coating by subsequent droplet deposition. This figure will also be discussed in more details in section 8.3.3.

![Figure 8-4. Evolution of pore size over time in the bottom and the top-spray coating processes (taken from analysis of samples from experiment BS1 and TS1).](image)

At the end (after 133 minutes) of coating process, pores were hardly visible in the coating film, including in the part of coating close to the core surface (see Figure 8-5). The porosity reduction via scenario 1 would never lead to the disappearance of pores in the inner part of the coating. The only way that pores reduced in size as well as disappeared at some point was due to the subsequent layering that resulted in an alteration of the morphology of the pre-existing coating layer. As mentioned before, this could occur either via pore-filling mechanism (scenario 2) or via rewetting of the pre-existing coating matrix (scenario 3).

The pore-filling phenomenon can however only occur if the pores are open *i.e.* located on the surface of the coating layer. This was only true for coating films made after a
short coating process time (see the CSLM images after 19 minutes of coating process in Figure 8-5). After longer coating time, most pores are located close to the core surface. The pore-filling mechanism can therefore only occur at the beginning of the coating process. As process continues, pores are mostly isolated, which means that the reduction of the pore size is no longer possible via the pore-filling mechanism.

![Figure 8-5. Spatial distribution of pores in the coating layer during the bottom-spray coating process (experiment BS1).](image)

To test the plausibility of the third mechanism, i.e. the rewetting of the coating matrix, experiments were performed by initially spraying an HPMC polymer solution and then shifting it to water and finally spraying the coated particles again with a HPMC solution. The experiments were performed using two HPMC concentrations: 5 and 10%, respectively. The results are shown in Figure 8-6. It can be seen here that after water droplets were sprayed, the coating porosity as well as the pore size do continue to reduce. It was also found to be consistent for both HPMC solutions. This finding supports the plausibility of the pore size reduction via the plasticization of polymer upon contact with moisture. After coating solution was sprayed again, the porosity and the pore size increased (see Figure 8-6). This increase was
actually due to the limitation in the minimum final porosity and pore size that could be achieved using the given formulation and process settings. For this reason, the final porosity and pore size of using 10% HPMC solution was higher than those using 5% HPMC solution, due to its inferior film formation properties, e.g. higher viscosity and therefore poor spreading.

**Figure 8-6.** Effect of switching the sprayed coating solution to water and back to coating solution on the porous structure of the coating layer: experiments BS7 and BS8, respectively.

The pore-size reduction via the rewetting mechanism also explains the higher pore size reduction in the bottom-spray than in the top-spray process, as in the bottom-spray process the droplets most likely contain higher moisture content than in the top-spray process. Accordingly, the droplets will rewet the precursor coating layer more intensely in the bottom-spray than in the top-spray coating process. To investigate the significance of the re-wetting mechanism of the precursor coating layer on the reduction in its pore size, experiments were performed by initially using top-spray nozzle and afterwards bottom-spray nozzle. The result is shown in Figure 8-7. It can be seen here that by changing the nozzle location from the top to the bottom of the bed in the middle of the coating process, both the final porosity and pore size decreased. The reduction however did not reach as low as the porosity and the pore size if a bottom-spray nozzle were used from the very beginning of the coating process. This shows the limitation of pore size reduction via re-wetting mechanism of the coating layer, which depends on the maximum polymer dissolved in the contacting
moisture. The conditions in which droplets dry and deposit on particles are by far also the determining factors of the final coating qualities (190).

Figure 8-7. Effect of switching from the top to bottom-spray nozzle on the porous structure of the coating layer (experiment TSBS1).

So far, it can be concluded that rewetting of the pre-existing coating matrix is the most plausible mechanism that causes the reduction of pore size and therefore the total porosity in the coating film after a sequence of layering. To facilitate this mechanism, the droplets ought to be wet enough to induce the re-dissolution and therefore the densification of the coating polymer. Such mechanism will not only affect the pore size but also the spatial distribution of pores in the coating films, which will be discussed in the following section.

8.3.3. The spatial distribution of pores in the coating layer

The location of pores in the coating film is given as the relative (shortest) distance of pores from the core surface i.e. the fraction of coating thickness, where “0” indicates the inner boundary and “1” the outer boundary. The fractions of pores at a certain distance from the inner boundary give the so-called spatial pore distribution in the coating layers, which are depicted in Figure 8-5 and Figure 8-8, for films made in a bottom-spray and a top-spray
system, respectively. Here, it can be seen that the relative distance from core surface that covers 50% of the total porosity ($X_{50\%,\text{por}}$) is less than 0.25 for films made using bottom-spray system and 0.26 for films made using a top-spray system. In other words, in both processes at least 50% of the pores are located close to the core surface.

![Graph showing cumulative fraction of porosity vs. relative distance from core surface](image)

**Figure 8-8.** Spatial distribution of pores in the coating layer during the top-spray coating process (experiment TS1).

At the beginning of coating process, the coating films made in the bottom and top-spray systems appeared to have comparable structures, shown in the comparable $X_{50\%,\text{por}}$ of films made after 19-20 minutes of coating. At this stage, there were only few layers formed on the particles and some parts of the particle surface are not yet covered by a coating film (see red arrow pointed to the inserted CSLM images in Figure 8-5 and Figure 8-8 of the particles coated for 19 and 20 minutes in the bottom and top-spray system, respectively). For this reason, the more “wet” situation in the bottom-spray system did not seem to help in achieving a denser coating film. Nevertheless, as the layering proceeds, the spatial pore distribution in the coating layer evolves differently in the bottom-spray than in the top-spray coating process.
In the bottom-spray coating system, the relative distance from core surface covering 50% of the total porosity ($X_{50\%}$) became significantly smaller with the increase of coating time, which shifted from 0.25 to 0.04 when coating process proceeded from 19 to 133 minutes. On the contrary, in the top-spray coating process, the $X_{50\%}$ only reduced from 0.26 to 0.18 when the coating process proceeded from 20 to 140 minutes. As mentioned previously, at the process settings used in the top-spray coating experiments, the droplets seemed to be not wet enough to induce the rewetting mechanism and the pore reduction is predominantly via the subsequent layering by a denser film on top of the previously formed film. The new layer was however most likely not so dense, considering the intense droplet drying in the top-spray system. For this reason, the pore structure comprising of the pore size distribution as well as the spatial distribution of the pores in the films made using a top-spray system did not vary greatly over the coating time.

**Figure 8-9.** The effect of inlet gas flow rate on the final spatial distribution of pores in the coating films made using bottom-spray (BS) and top-spray (TS) coating processes: experiments BS6, TS3, BS3 and TS2, respectively. The inserted table gives the relative distance from core surface covering 50% of the total porosity ($X_{50\%}$).

Figure 8-9 and Figure 8-10 show further the impact of variation in the inlet gas flow rate and atomization pressure, respectively, on the spatial distribution of pores in the coating layers. The results revealed that the effect of the inlet gas flow rate is only significant on the
spatial distribution of pores in films made in the bottom-spray coating process (see Figure 8-9). It is shown that more pores are concentrated in the inner part of the coating and less are found close to the surface of the coating film, where $X_{50\%,por}$ shifted from 0.08 to 0.05, when the gas flow rate was increased from 20 to 25 m$^3$/h. At higher gas flow rate, the particle velocity is increased and thus the circulation time of the particles is reduced. At similar duration of coating process, a shorter circulation time will lead to a higher number of layering cycles. For this reason, the inlet gas flow rate led to similar effect as the coating time on the evolution of size distribution as well as spatial distribution of the pores. For a top-spray coating process, where rewetting is not a predominant mechanism, changing gas flow rate gave a little effect, as confirmed in the constant values of $X_{50\%,por}$ at 0.3 when the gas flow rate is increased from 20 to 25 m$^3$/h.

Figure 8-10 shows the effect of atomization pressure on the final spatial distribution of pores throughout the coating films. A higher concentration of pores in the inner part of the coating films was obtained with the increase of the atomization pressure from 0.5 to 1.5 bar, shown as a shift of $X_{50\%,por}$ from 0.12 to 0.05 at spraying rate of 2.4 g/min, respectively.

**Figure 8-10.** The effect atomization pressure on the final spatial distribution of pores in the coating films made using a bottom-spray coating process (experiments BS1-BS5). The inserted table gives the relative distance from core surface covering 50% of the total porosity ($X_{50\%,por}$).
At a low atomization pressure, the coverage rate of the particles is significantly lowered, due to the bigger size of droplets produced. Using similar spraying rate, at a low atomization pressure, the number of droplets sprayed is lower than that at a high atomization pressure. Accordingly, it takes longer time for completing a layering cycle of a particle when a low atomization pressure is used. At this atomization pressure, the coating layer was rewetted less often than when a high atomization pressure is applied at similar coating time. This effect was found to be consistent for different spraying rate used, where \( X_{50\%,\text{por}} \) is shifted from 0.25 to 0.05 at spraying rate of 4.8 g/min. At high spraying rate, in fact the effect of atomization pressure (droplet size) becomes more obvious on the spatial distribution of pores in the coating layer. This is correlated to the significant increment of the droplet size and therefore higher reduction in layering sequence attained at high spraying rate.

8.4. Conclusions

The quantification of pore structure of the coating films, entailing the total porosity, the pore size distribution and also the spatial distribution of pores has been presented. This information is not only important to predict the coating performance but also to optimize the process parameters, such as the coating time, the position of nozzle, the inlet gas flow rate and the atomization pressure.

The analysis of pore size distribution in the coating films taken at various process times provides better understanding of the relevant mechanisms of the film formation in a fluidized bed coater that determine the final coating structure. For processes where droplets are wet enough when they reach the particles, re-wetting of the polymer by moisture in the droplets is shown to be predominant in causing the reduction of pore size and therefore the total porosity. The analysis of the spatial pore distribution also supports the plausibility of this mechanism, where pores in the outer part of coating films were found to disappear first. As the pore size reduces gradually, sufficient coating time or layering cycles are required to achieve the minimum porosity and pore size at any given process settings. To facilitate sufficient layering cycles, the inlet gas flow rate as well as the atomization pressure should also be optimized.
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