

Microencapsulation and surface passivation fine porous particles

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1. Introduction

Encapsulation technology has been used in industries such as food, pharma, and agrochemical for many years¹ with the purpose to protect the active ingredients and release them in a desired manner when needed. For an increased product efficiency, the encapsulated active ingredients have to be protected not only from the **external environment** but also from the **internal supporting structure** (pore surface). This is particularly the case of active ingredients loaded in porous media that display highly reactive species at the surface. This can lead to chemical degradation of the active ingredients in time, thus, less effective, and shorter storage lifetime products.

Additional difficulties come with the **size of the particles** that need protection. Indeed, the coating process on fine particles is not straight forward, rendering the coatings intended to suppress volatility, flavor, odor, or sensitivity to light (or moisture) a real challenge. Essentially, the smaller the particles the more difficult is to control the coating process, and for particles below 50 microns it is **almost impossible** to do that with common technologies such as fluid bed coating². This sets a clear restriction for product developments for food, pharma, and agrochemical industries.

In summary, for **fine particles** to be suitable carrier and delivery media for sensitive ingredients there are two challenges to be addressed. First, improved protection from the internal pore walls by **surface passivation**; and second, improve protection from the external environment by **coating the entire particle** after loading with the active ingredient. Both tasks could essentially be addressed by using the supercritical (sc) CO₂ medium: surface passivation in a first step followed by particle coating in a second step.

2. Materials and Methods

The particles to be surface passivated (or coated - encapsulated) are immersed in a solution of the polymer to be used for surface passivation (or particle coating). This is placed inside the reactor and then CO₂ is gradually added. The **CO₂ is used as an antisolvent**, meaning that the coating polymer, formerly dissolved in a solvent, precipitates when interacting with CO₂. It is important to note that the solvent (dissolving the polymer) and the antisolvent (CO₂) are miscible.

As model host particles, or carriers, we have used porous silica particles, brand name Syloid (about 3 microns in size), and porous Kromasil particles (7 microns in size) to demonstrate the ability of surface passivation. For demonstrating the ability for overall coating, we have used dense cellulosic particles - brand name Cellets (about 350 microns in size). For both surface passivation and overall coating, we have used the following polymers: hydroxy propyl cellulose (HPC), ethyl cellulose (EC) and Eudragit (L100 and L100-55).

As solvents for the above-mentioned polymers, we have used Ethanol and Toluene/Ethanol mixtures. The change in the pore volume and surface area before and after polymer treatment was measured using BET (Brunauer-Emmett-Teller) method and for imaging Scanning Electron Microscope – SEM was used. The pressure in the reactor varied between 55-100 bar while the temperature varied between 22-50 degree C.

3. Results and discussion

Surface passivation. Syloid particles were treated with 4wt% of each of the following polymers: Eudragit, HPC and EC. Kromasil particles were treated with only Eudragit polymers at 4wt%, 20wt% and 33wt%. Here only representative results are presented. As expected, the SEM images of Syloid particles (not shown here) before and after polymer treatment do not differ at all because the polymer precipitated inside the pores, likely on the pore walls. This result was confirmed by the BET measurements, presented in Table 1, which clearly show **drop in surface area** when treated with 4wt% polymer as compared to reference. The

same trend was observed for Kromasil, presented in Table 2. The data shows that with increasing the total content of Eudragit polymer both the external surface area and the specific surface area (BET) are shrinking as compared to untreated material (reference) demonstrating the increased thickness of the deposited polymer layer. Here, however, due to the regular shape of the particles, one could observe the presence of the polymer at high polymer concentrations as noticed in Figure 1a.

Table 1.

Syloid system	Reference	4wt% L100-55	4wt% EC N10
Ext. surface area [m ² /g]	342	280	295
SSA (BET) [m ² /g]	351	313	321

Table 2.

Kromasil - Eudragit	Reference	4wt%	20wt%	33wt%
Ext. surface area [m ² /g]	269.6	211.4	174.6	130.9
SSA (BET) [m ² /g]	310.0	214.7	189.7	137.5

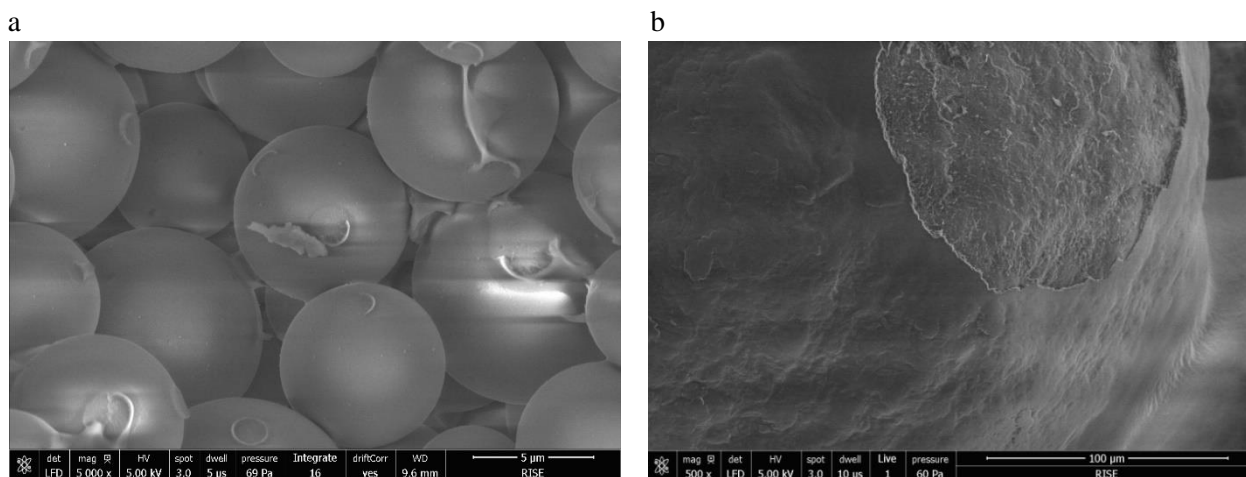


Figure 1. SEM images of a) Kromasil pore surface modified with Eudragit and b) Cellets overall coated with HPC.

Overall surface coating. In this case Cellets particles were treated with HPC, Eudragit, and EC polymers at varying coating weights (from 2-50wt%). In Figure 1b is presented a coating with 4wt% HPC which shows the ability cover the particle with a tiny polymer layer. The crater visible in the upper right part of the image is likely a mark of a rupture from an adjacent particle. Additionally, from 2-33wt% a good flowability of the particles after polymer treatment was obtained. However, this parameter seems to be dependent on the CO₂ exposure time, the ratio between solvent and antisolvent (CO₂), and ability to extract the solvent of the polymer.

4. Conclusions

In this work we have demonstrated that scCO₂ has the ability to both **surfaces passivate** fine porose particles and lay an **overall coating** on dense particles. First, by surface modifying the interior of porose particle, that is depositing a polymer layer on the pore walls, one could eventually protect sensitive ingredients that are loaded in this media from the active species present on the internal pore wall. Second, by laying an overall coating on particles loaded with active ingredients one could protect the active ingredients from external stimuli as well as control their release. Our vision is to scale up these results into **industrial processes that could stimulate growth** in the food, pharma, and agrochemical industries.

Acknowledgements

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References:

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