

INVESTIGATION OF COATINGS PRODUCED IN A HIGH PRESSURE FLUIDIZED BED

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In this process, supercritical carbon dioxide is continuously saturated with a coating material and then expanded into a high pressure fluidized bed which is operated with supercritical CO₂ as well. Uniform, thin and solvent free wax coatings were successfully produced on various particles. In this work, interfacial forces, viscosities as well as contact angles of the system CO₂-wax with different solid materials were measured. According to the results of these measurements and the theory for the formation of liquid bridges it was found that the agglomeration tendency is lower at supercritical fluid conditions inside the fluidized bed. At the same time the yield of the coating process decreases with increasing pressure. These findings were confirmed with coating experiments of aluminum nitride particles and results of our previous work.

INTRODUCTION

The coating of particles has its applications in the protection of high value products, the encapsulation of hygroscopic or toxic substances, and the pharmaceutical industry, where a selective or controlled release of a drug is demanded. In previous studies it was demonstrated that the combination of the fluidized bed technique with the use of supercritical carbon dioxide enables the production of complete, thin, uniform, and solvent free coatings [1,2]. The procedure is based on a RESS process with the difference that a homogenous solution of supercritical CO₂ and the coating material is expanded into a fluidized bed, which is operated at supercritical fluid conditions as well. Because of the pressure difference due to the expansion the solubility of the coating material changes drastically and droplets precipitate in the vicinity of the nozzle. It was shown that it is possible to adjust the coating's morphology by varying the process parameters. A maximum yield of about 90 % and a coating thickness of 0.7- 2.0 μm were obtained. In screening tests, various particles with a size of about 38 – 200 μm were encapsulated with paraffin waxes typically used in technical coating applications. Glass beads, ceramic beads, potassium chloride crystals, plastic granulate and lactose agglomerates were used. The present work is focused on the influence of the supercritical fluid conditions in the fluidized bed on the coating process. Therefore interfacial forces, viscosities as well as contact angles of the system CO₂-wax with the respective solid materials were measured. In addition, the findings based on the investigations of the physical properties of the systems were tested with a new application, the coating of aluminum nitride particles by varying the operating pressure in the fluidized bed.

THEORETICAL BACKGROUND

Four important factors for the evaluation of a coating process can be defined. These factors will be explained and discussed related to the used high pressure fluidized bed coating process in the following section. Primarily, the distribution of the coating material in the fluidized bed needs to be uniform. Important for the uniform distribution is a good mixing of the particles. In general, the solid mixing in fluidized beds is very good. Hydrodynamic investigations of

the high pressure fluidized bed were performed by our co-operation partner [3,4]. The hydrodynamic behavior is influenced by the operating pressure and the temperature of the fluidized bed. A bubbling behavior and thus a good solid mixing is found at lower operating pressures depending on the density and size of the used particles. Secondly, the yield of the coating defined as the amount of the coating material on the particles in comparison to the used material has to be high. For expensive or hazardous substances a high yield is demanded. The yield is low if the coating material does not adhere to the core particle or solidifies before hitting a particle. The solidification time is influenced by the size of the wax droplets produced during the expansion. The solidification temperature and the crystallization enthalpy of the coating material are of influence as well. Our previous work has shown that the solidification temperature and the crystallization enthalpy of the paraffin decrease with increasing pressure due to the increase of the solubility of carbon dioxide in the paraffin [1]. The third factor for the evaluation of coating processes is the thickness of the coating. A flexible and precise control of the layer thickness is desirable. It is mainly influenced by the interfacial forces between the coating material and the surrounding fluid and by the contact angle of all three apparent phases. Finally, the agglomeration tendency is crucial for the coating process. Whereas a high agglomeration tendency is favored for granulation processes agglomeration needs to be avoided for coating processes. Rumpf has investigated the adhesion forces between particles [5]. They found that van der Waals forces and electrostatic forces are less important for the adhesion of particles than the liquid bridges formed by the coating material. The strength of liquid bridges is mainly given by the capillary pressure p_c inside the liquid bridge and thus it is influenced by the curvature of the liquid between the particles. A simplified equation for the adhesion force between particles due to liquid bridges can be written as follows [6]:

$$p_c = \cos(\mathbf{q}) \cdot \mathbf{s}_{lg} \cdot \frac{6}{\mathbf{y} \cdot d_p} \cdot \frac{1 - \mathbf{e}}{\mathbf{e}} \quad (1)$$

where d_p is the particle's surface mean diameter, ψ is the sphericity and ϵ is the porosity of the bulk. Equation 1 shows that the adhesion force decreases with decreasing interfacial forces between the coating material and the fluid and with increasing contact angle.

Ennis et al. investigated granulation processes in fluidized beds and they made a different approach for the adhesion force between the particles [7]. They have shown that the viscosity of the binder liquid is more important for the strength of the liquid bridge than the adhesion force caused by the capillary pressure inside the bridge. During the impact of two particles covered with a liquid layer kinetic energy is dissipated due to the viscosity of the liquid. Ennis et al. defined a critical viscose Stokes number for this dynamic liquid bridges which depends on the coefficient of restitution e , the thickness of the liquid layer s and a mean height of an increment on the particle h_a :

$$St_v^* = \left(1 + \frac{1}{e}\right) \cdot \ln\left(\frac{s}{h_a}\right) \quad (2)$$

The viscose Stokes number has to be larger than this critical Stokes number ($St_v \gg St_v^*$) for coating applications. Otherwise granulation or agglomeration would occur.

$$St_v = \frac{4 \cdot \mathbf{r}_p \cdot u_0 \cdot d_p}{9 \cdot \mathbf{m}} \quad (3)$$

where ρ is the particle's density, μ the viscosity of the coating material and u_0 the approach velocity of the particles. Hydrodynamic investigations have shown that the bubbles formed in

a high pressure fluidized bed are faster and smaller than under atmospheric conditions [3]. Thus the velocity u_0 is higher, the viscose Stokes number is increased and coating is favoured.

Although the viscosity is important in case of moving particles, the adhesion because of static liquid bridges can not be neglected for the described process. Areas in the fluidized bed exist where the particles do not move for a short time. Furthermore, the adhesion force due to the capillary pressure is always present when liquid bridges occur. The described factors show that the knowledge of the viscosity, the interfacial forces and the contact angles is crucial for the performance of a coating process.

INVESTIGATION OF THE PARAFFIN-CO₂-SYSTEM

The viscosity of the paraffin rich phase in the system paraffin-CO₂ was investigated for isothermal conditions (70°C) in a pressure range of 0.1-25 MPa using a high pressure ball viscosimeter (Co. Ruska). For detailed descriptions see [8]. The paraffin ($T_m=60^\circ\text{C}$, Merck AG) saturated with carbon dioxide (3.5, Co. KWD). was filled into the viscosimeter with an inner diameter of 8 mm and a length of 200 mm. The viscosity was calculated from the measured time the ball (\varnothing 5 mm) needs to pass a known distance inside the autoclave.

The interfacial forces between the paraffin rich phase and the CO₂ rich phase in the system paraffin-CO₂ were measured with the hanging droplet method, which is described elsewhere [8]. A high pressure view cell with a volume of 25.5 ml was used to perform measurements at 60 and 70°C in a pressure range of 0.1-25 MPa. The hanging droplet was produced with a screw press and a capillary with an inner diameter of 0.25 mm. The digitized images of the droplets were analyzed with a computer program („Drop Shape Analysis“, Co. Krüss) that calculates the interfacial forces from the shape of the drop.

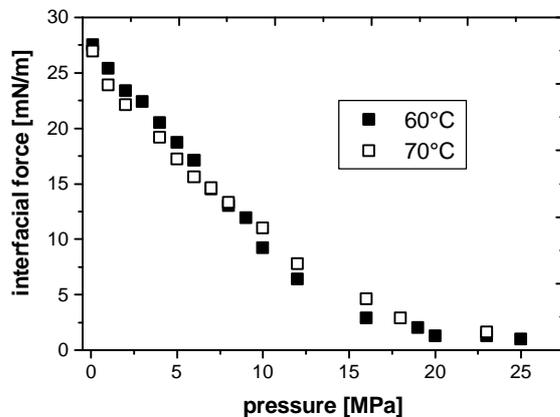


Fig. 1: Interfacial forces of the system paraffin-CO₂, T=60, 70°C

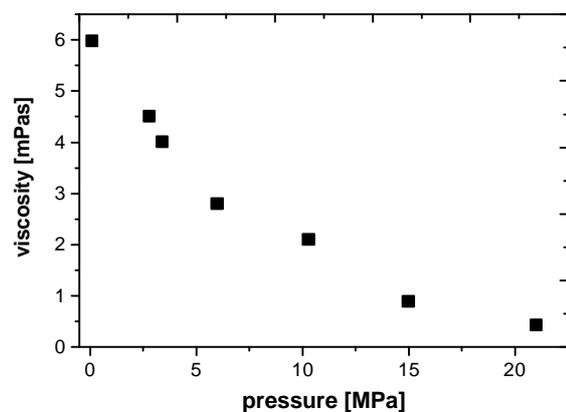


Fig. 2: Viscosities of the paraffin rich phase in the system paraffin-CO₂, T=70°C

The results of both measurements show, that with increasing pressure and carbon dioxide content in the paraffin phase the interfacial forces as well as the viscosities decrease (Fig. 1, Fig. 2). Similar observations were made for polymeric and oily systems [8,9,10].

According to equation 1 the adhesion force between particles due to static liquid bridges decreases with decreasing interfacial forces and equation 3 shows that the adhesion force due to dynamic liquid bridges also decreases with decreasing viscosity. Thus the agglomeration tendency should be lowered with increasing pressure.

INVESTIGATION OF THE SYSTEM PARAFFIN-CO₂-PARTICLE

The investigation of the contact angles was performed with the same autoclave used for the measurement of the interfacial forces. Two different methods were used. 1. Plate method: The

contact angle θ was derived from the height difference of the paraffin rich phase at a vertical plate in comparison with the level a few millimeters away from the plate [11]. Glass (Microscope slides) and porous ceramic plates (Al_2O_3 , pore diameter $5\ \mu\text{m}$) were investigated with this method. 2. Bulk method: A bulk of particles was filled into the view cell. The capillary height of the liquid phase in this bulk gives information about the contact angle [12]. Glass beads (Co. ASIKOS Strahlmittel GmbH) with a surface mean diameter of 2 mm and a bulk porosity of 0.35 were used.

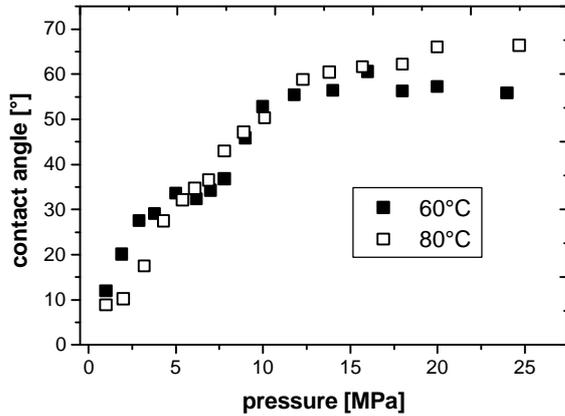


Fig. 3: Contact angles of the system paraffin- CO_2 -glass, plate method

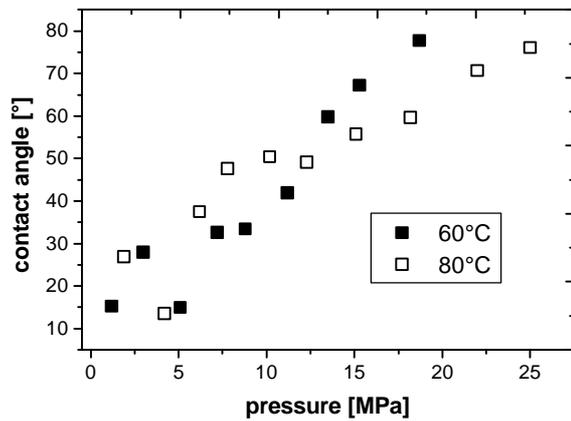


Fig. 4: Contact angles of the system paraffin- CO_2 -glass, plate method

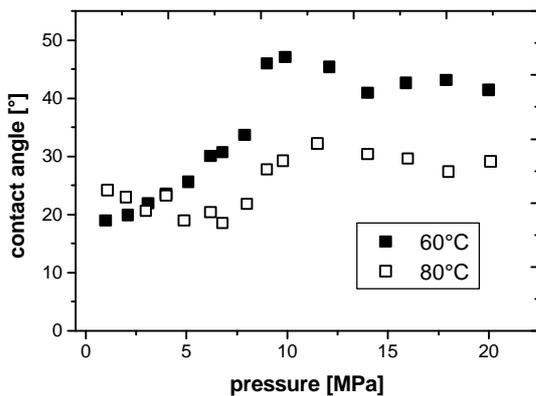


Fig. 5: Contact angles of the system paraffin- CO_2 -ceramic, plate method

The results of both measurement techniques show that the contact angle increase with increasing pressure (Fig. 3, Fig. 4). The temperature influence is small for the smooth glass surface. Similar observations were made by Wesch et al. [13]. The comparison of both methods shows that the measurement error for the “bulk method” is higher than for the “plate method”. Furthermore, for large contact angles above 60° the error made by the assumption of a constant bulk porosity becomes dominant leading to overestimated values. In the “bulk method” the particles utilized in the process can be investigated directly whereas in the “plate method” a plate with a similar composition is used.

In comparison the smooth glass surface the porous ceramic surface shows higher contact angles at lower pressures and vice versa under high pressures (Fig. 5). The temperature has an influence on the contact angle because smaller contact angles were measured at higher temperature. The reason is the enhanced wetting behavior of the porous structure due to the lower viscosity of the paraffin rich phase at higher temperatures.

In general the experiments show, that the wetting is sufficient ($\theta < 90^\circ$) under high pressure although the contact angle increases with increasing pressure. According to equation 1 the adhesion force between particles due to static liquid bridges decreases with increasing contact angle. Thus the coating is favored with increasing pressure. Furthermore, the agglomeration tendency should be lower in case of smooth surfaces like the glass in comparison to porous surfaces like the ceramic.

COATING EXPERIMENTS

Experiments were performed with highly water sensitive aluminum nitride particles (grade KT, Co. H.C. Starck) which, when sintered, are used in heat transfer applications in the semiconductor industry. The fluidized bed pressure was varied from 8 to 10 MPa. All other parameters were kept constant. The temperature inside the bed was 40°C whereas the expanded paraffin-CO₂ mixture had a temperature of 60°C. The pre-expansion pressure was set to 24 MPa leading to a wax content in the spray of 0.91 wt-% and a mass flow through the nozzle of 0.5 g/s. The fluidization velocity was twice the minimum fluidization velocity. The particles were sieved to particle sizes of 63-100 μm.

Tentative experiments verify the theory that the agglomeration tendency is lowered by increasing fluidized bed pressures. Whereas agglomerates (5-10 mm) were formed at 8 MPa, hardly any agglomerates were found when using a fluidized bed pressure of 10 MPa. Our previous work has shown that no agglomerates were formed with smooth glass surfaces at 8 MPa. Again, the observations from the measurements of the contact angles were confirmed. The contact angle on smooth surfaces is higher than on porous surfaces and thus the agglomeration tendency is lowered.

The yield of the coating process was determined with burn of experiments of the product [1]. The yield was about 100% for the agglomerated product and about 40% for the product realized at 10 MPa. Due to the lowered interfacial forces at higher pressures smaller droplets were formed. Thus the solidification time gets shorter and more solidified paraffin particles leave the fluidized bed together with the fluidizing gas stream.

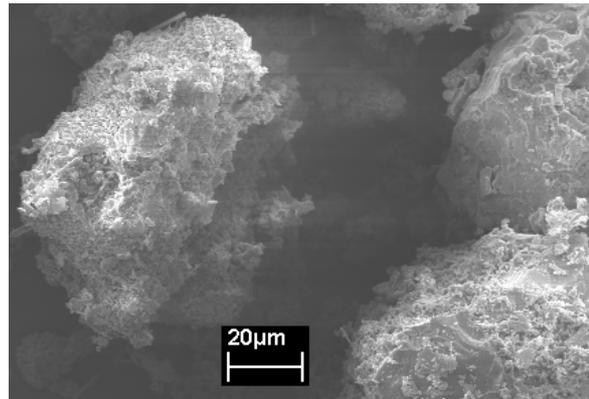
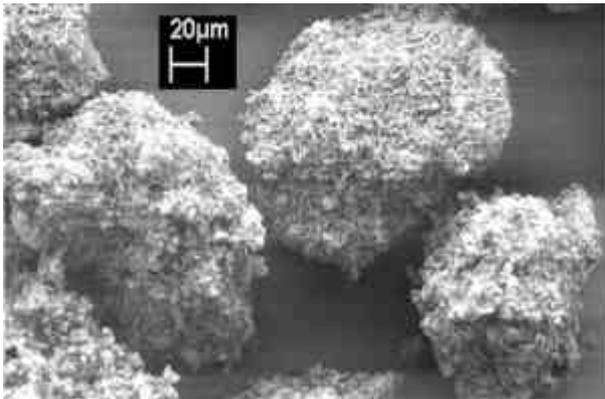


Fig. 6: Original aluminum nitride particles **Fig. 7: Coated aluminum nitride particles**

A comparison of the SEM (Scanning Electron Microscope) images of the raw material and the product show that the whole porous structure of the particle is covered with a thin layer of paraffin (Fig. 6, Fig. 7). The thickness of the coatings was found to be the same at 8 and 10 MPa. This observation can be explained with the measurements of the contact angle and the interfacial forces. The layer thickness increases with decreasing contact angle and with increasing interfacial forces. The increased pressure leads to decreased interfacial forces and to increased contact angles. Thus the effects cancel each other out.

CONCLUSION

The performed measurements show that the interfacial forces of the system paraffin-CO₂ as well as the viscosity of the paraffin rich phase of this system decrease with increasing pressure. At the same time the contact angle on ceramic and glass surface increases. The contact angles at the porous ceramic surface were smaller than at the smooth glass surface. It was demonstrated that basic tendencies for the wetting and thus the formation of the coating

can be derived from these investigations and from the theory for static and dynamic liquid bridges. Coating experiments with aluminum nitride particles at 8 and 10 MPa confirm that the agglomeration tendency is lowered by increasing the pressure. Due to the decreased interfacial forces smaller droplets were formed at higher pressure leading to a decreased yield at a pressure of 10 MPa. Furthermore, in agreement with theory, the agglomeration tendency was higher for the porous aluminum nitride surface than for a smooth glass surface.

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