

# Micro Particles Filled with Liquid Using the Particles from Gas Saturated Solutions Technology

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Classical methods offer many possibilities to generate powders. Where very small particle sizes especially in spherical shape are required, or highly viscous substances have to be reduced, the limits of traditional processes are reached soon. The solution can be found in high-pressure processes. The **PGSS (Particles from Gas Saturated Solutions)** process e.g. is suitable for the micronisation of several substances. With a couple of investigations it could be proved that fine powders with different morphologies can be manufactured [1-3].

The possibilities of the PGSS process have successfully been demonstrated over the last years for numerous solids such as e.g. polyethylene glycols, powder coatings and green tea. The aim of this investigation was the production of liquid filled powder micro particles using the PGSS process. This way the encapsulation of a dispersed liquid phase was achieved and powders with different properties were produced. The properties of the composite powders can be adjusted by the process parameters of the PGSS process. Products with different morphologies, particle sizes and bulk densities can be manufactured.

## INTRODUCTION

One of the basic requirements of marketing is to have new and innovative products. At the same time the costs for the production of these new products are expected to decrease. Powderous composites satisfy numerous of these requirements. Solid as well as liquid resources are transferred into a form, which is easy to dose, mixable and stable e.g. by binding a liquid into a composite. Even special release behavior of the resources can be achieved by changing the composite morphology or the composite shell material. These powder composites can be used as products in various industrial sectors. An interesting field of use for these products is the production of intelligent materials for buildings: **PCMs (Phase Change Materials)**. PCMs effectively save energy by storing or releasing energy during phase change. They can be used e.g. for air conditioning purposes. The binding of the phase change material is necessary to prevent the liquefied PCM from leakage. Another interesting application, e.g. for the food industry, is the encapsulation of aqueous solutions in fats [4].

Powder composites can be produced by chemical and physical processes. The field of chemical processes has been well investigated and described in literature [5-8]. Physical processes are traditionally methods based on impregnation, precipitation, solidification and drying [9-12]. Physical high-pressure processes for composite production offer a new possibility for composite generation and are investigated for the PGSS process in this research.

The term composite, as it is used in this article, describes a mixture of at least two substances. The liquid is often called core material in this article and has to be bound and/or encapsulated by another substance, which is called shell material. The morphologies of such compounds can be classified into open and closed composites. Open composites are characterized by a contacting surface of bound substance (liquid) and surrounding atmosphere, while the liquid in closed composites is completely surrounded by shell material.

## **I - MATERIALS AND METHODS**

### ***Experimental Setup***

Using the PGSS process for the generation of composites, a shell material is filled into, heated and molten in a vessel. The liquid is filled into another vessel and heated. Both materials are pressurized and dosed to a mixing system. In the mixing system micro droplets of the core material are dispersed in the liquefied shell material. A supercritical fluid is added and partly dissolved in the formed emulsion. The dispersion is expanded to ambient pressure through a nozzle into a spray tower. Fine droplets are formed by the expansion. Simultaneously the drops are directly cooled by the expanding gas (Joule Thomson phenomenon). The shell material solidifies and forms a cover around the micro liquid drops, thus generating a powderous composite. Maximum operating pressure and temperature of the used plant are 350 bar and 200 °C, the maximum mass flow is approximately 50 kg/h for shell material, 10 kg/h for core material and 150 kg/h for fluid (fluid measured with Coriolis flow meter, shell material and liquid measured with differential weighing).

### ***Material combinations***

In this investigation, two different liquids were used. The first, a liquid paraffin, was bound in a polyester. Handmade mixtures of this polyester/paraffin system are extremely instable and break within a few seconds. The polyester, a linear copolyester, is partially crystalline with a melting point of approximately 96 °C and an average density of 1190 kg/m<sup>3</sup> under room conditions. The paraffin has a melting point between 5 and 7 °C and a density of 860 kg/m<sup>3</sup> in solid conditions.

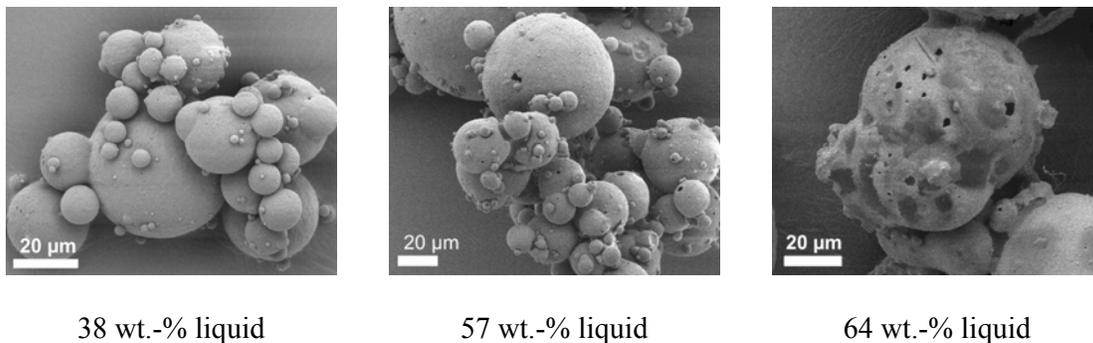
The second liquid, a liquid polymer (PEG), was bound with the use of different waxes. The handmade mixtures of the wax/PEG systems form more stable emulsions than the polyester/paraffin systems. The waxes have a drop point between 98-120 °C and a solid density of 940 to 960 kg/m<sup>3</sup>. The liquid polyethylene glycol has a melting point between 4 and 8 °C and a solid density of 1200 kg/m<sup>3</sup>.

The particle size distribution of the produced powders was measured in dry state by laser diffraction, using a Malvern Mastersizer 2000. The bulk density was measured by weighing a known powder volume. The mass fraction of liquid in the composites was calculated by the liquid mass flow divided by the sum of the liquid and the shell materials mass flow, assuming that vapor pressure of the liquid at spray tower conditions (low temperatures and atm. pressure) as well as solubility in gaseous fluid are negligible. The particle morphology was judged with the help of photos from a scanning electron microscope (SEM).

## **II - RESULTS**

### ***Morphology***

The particle morphologies observed in this investigation vary between agglomerates and spheres in outer shape. Open structures as well as completely closed structures can be found. The photos of some wax/PEG composites are shown in figure 1. In the picture the liquid appears in the picture with a dark-grey color and the light grey colored regions consist of shell material.

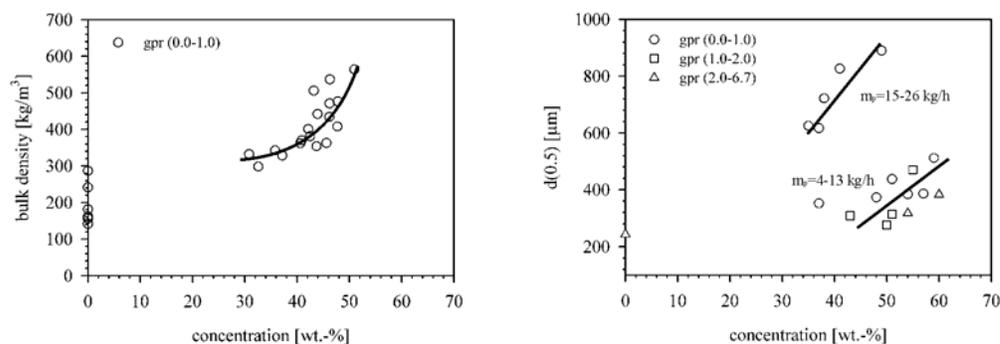


**Figure 1:** SEM pictures of composite particles (wax/PEG system)

In figure 1 closed composites, agglomerates and porous particles filled with liquid (PEG) are displayed. Generally, it was found that with increasing concentrations of liquid the formation of open composite is favored. The change from closed to open composites in the wax/PEG systems seems to start at a liquid fraction between 50 and 60 wt.-%. The change from closed to open composites in the polyester/paraffin system begins earlier, it occurs in the range of 40 to 50 wt.-% of bound liquid.

**Bulk density and particle size**

In the polyester/paraffin system, a rising concentration of liquid causes a rising bulk density. At low liquid fractions the increase is moderate and accelerates with rising values. Figure 2, left side, shows the bulk density of the polyester/paraffin system (experiments without any liquid are displayed on the y-axis, the variation of the values is a result of the variation of the experimental parameters: e.g. temperature, pressure and mass flows) versus the concentration of liquid. Although the parameters of the displayed experiments have been varied over a wide range the experiments demonstrate an influence of the concentration on the bulk density. Consequently, the liquid concentration is a dominating parameter. A significant rise of the bulk density can already be observed at concentrations above 30 to 40 wt.-% liquid (figure 2, left side). In contrast, the experiments of the wax/PEG system show nearly no influence of the concentration of PEG on the bulk density at low to moderate values of the concentration. Only at high concentrations a very slight rise of the density can be assumed.



**Figure 2:** Bulk density versus concentration for the polyester/paraffin system (left side) and particle size as d(0.5)-value versus concentration of the polyester/paraffin system (right side).

The particle size distribution of the polyester/paraffin powders strongly depends on the sum of the liquid and shell material mass flow (particle mass flow,  $m_p$ ), the concentration of the bound liquid and the gas-to-product ratio (gpr). The gas-to-product ratio is calculated by the mass flow of the fluid divided by the particle mass flow. In figure 2, right side, the particle sizes of the experiments (shown in form of  $d(0.5)$ , which means 50 % of the particles are smaller than the indicated value) versus the liquid concentration are displayed for different ranges of the particle mass flow as well as the gas-to-product ratio. A rising particle mass flow and a rising concentration of the liquid result in growing particle sizes.

### **III - DISCUSSION**

#### ***Morphology***

For the morphology, it was found that a rising concentration of the liquid favors the generation of open composites. This can be understood focusing on the basic principles of particle formation. To form a composite the liquid has to be admixed to the shell material to form an emulsion. Subsequently this emulsion is sprayed and solidified. The decisive factor for the generation of closed or open composites is the velocity difference of the solidification and the phase separation of the emulsion. A rising amount of dispersed liquid drops in the emulsion leads to an accelerated phase separation of the emulsion. In addition, an increasing amount of liquid results in a rising drop diameter of the disperse phase. An increasing drop diameter of the disperse phase favors the phase separation of the emulsion. An accelerated phase separation leads to the generation of more open composites.

#### ***Bulk density and particle size***

The increasing bulk density at higher values of the concentration can easily be explained by the generation of open composites. SCHUBERT and WEIGERT describe the formation of particles by agglomeration [13, 14]. A liquid uptake by agglomeration will mainly cause a rising bulk density. This effect was e.g. confirmed by LANKES [15].

The PGSS process comprises an agglomeration as well as an encapsulation process step. For small amounts of liquids an encapsulation in the shell material will be easily achieved. This leads to an extension of the particle formation steps as described by SCHUBERT and WEIGERT. This extended scheme is characterized by the formation of closed composites in the beginning (step 1), which leads to a bulk density dependency caused mainly by the density differences of the core and the shell material. The sequential dependencies (step 2) should be characterized by a rising bulk density. By switching to more stable emulsions (wax/PEG systems) a rising concentration value for the change from step 1 to step 2 is effected.

The particle size depends on the particle mass flow, the gas-to-product ratio and the concentration of the bound liquid. The particle mass flow is the dominating parameter here. A rising particle mass flow leads to a rising particle size. This is caused by an agglomeration process in the spray tower. By increasing the particle mass flow the probability of collisions of not completely solidified particles rises which results in bigger particles.

### **IV - CONCLUSION**

The PGSS process can be used to generate open and closed composites out of stable (wax/PEG) and instable (polyester/paraffin) systems. A rising amount of liquid concentration

favors the formation of open composites and leads to a rising bulk density. The stability of the system is a critical factor which leads to the formation of closed or open structures. A better stability of the emulsion supports the encapsulation and therefore allows higher liquid concentrations in the composite.

The described process principles have meanwhile been applied to many combinations of liquids and shell materials. Powders with shell materials like natural or synthetic organic polymers, fats and waxes and liquids like soy sauce, water and liquid polymers have been produced. Dry and free flowing powders with over 60 wt.-% liquid (soy sauce in hardened fat) were achieved. It was shown, that a significant portion of the liquid remains steadily encapsulated in the powder [4].

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