

Nanoscale Plasma Surface Modification of Powders

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ABSTRACT

The plasma downstream reactor is designed to deposit nanostructures on substrate particles, to improve substrate powder properties as flowability, compactibility, wettability or the dissolution rate. The nanostructures are produced from an organosilicon monomer and directly attached on the substrate particle surface by plasma enhanced chemical vapor deposition in one process step of approximately 0.1 s. The low-temperature plasma enables to modify also temperature sensitive materials such as pharmaceuticals, polymers or nutraceuticals. The amount, size and chemical composition of the emerging nanoparticles is influenced by the process parameters such as system pressure, plasma power, residence time or the gas composition. This facilitates to tailor the final powder properties. In this paper the influence of the process pressure on the nanoparticle production and final powder properties is exemplarily shown.

Keywords: plasma downstream reactor, particle surface modification, nanoparticle formation, plasma, flowability

1 INTRODUCTION

Many products and intermediates in chemical, pharmaceutical or food industry exist in the form of powders with a typical median particle size in the low micrometer range. But already basic unit operations such as conveying, dosing or mixing become a challenge as soon as the particles are small and cohesive. The handling performance of such powders strongly depends on wettability, flowability and compactibility of the particles.

These properties of the microscopic particles can be improved by plasma-induced surface modification. For this, the powders are treated in a plasma downstream reactor (PDR) which provides fast (0.1 s) and homogeneous treatment of the particle surfaces [1]. SiO_x nanoparticles are generated from organosilicon monomers in a low-temperature plasma and simultaneously attached to the surface of the substrate particles. These synthesized nanoparticles act as spacers between the substrate particles and thereby improve the powder flowability as the attractive interparticle Van der Waals forces are reduced [2,3].

Depending on the process conditions and the choice of monomer the modified powders become hydrophobic or

hydrophilic. This enables to control the flowability, compactibility, wettability and thus also the dissolution rate of a compound by one single, very fast and quasi-continuous process.

In this study lactose is used as a test substance due to its similarity to many pharmaceutical products. If no substrate powder is feed to the reactor, SiO_x nanoparticles are produced in a pure form and its morphology, chemical structure and production rate can be studied as a function of the process parameters.

2 EXPERIMENTAL

The process scheme and a sketch of the plasma chamber are illustrated in Figure 1. The plasma chamber (1) consists of a double wall glass reactor with an inner diameter of 40 mm. The gap between the tubes is filled with water (2) for temperature control. The discharge is driven by an inductively coupled plasma (ICP) source which operates at a radio frequency (RF) of 13.56 MHz and a forward power of 300 W. The RF-generator (3) is connected over a matching network (4) with the water cooled copper coil (5) on the outside of the cooling jacket. As a test substance lactose powder (GranuLac 200, Meggle, Germany) is fed from the storage container (7) over a metering screw (8) to the downer pipe and mixed with the process gases oxygen, argon and the evaporated organosilicon monomer (6) in a nozzle (9). Below the plasma zone the particles are separated from the gas stream by a downcomer (10), cyclone (11) and filter unit (12) and collected in the solid collection vessels (13). A constant pressure of 200 Pa in the reactor is maintained during the process by a butterfly control valve (14) in front of the two stage vacuum pump (15).

2.1 Electron Microscopy

The pure SiO_x nanoparticles are analyzed by transmission electron microscopy (TEM) using a Philips CM 12 microscope at an acceleration voltage of 100 kV. The nanoparticles are directly collected on a copper grid, which can be placed in front of the filter (12).

2.2 Gravimetric Analysis

The amount of nanoparticles produced is measured by weighting the polyester filter (Type: TFV 478/170 A,

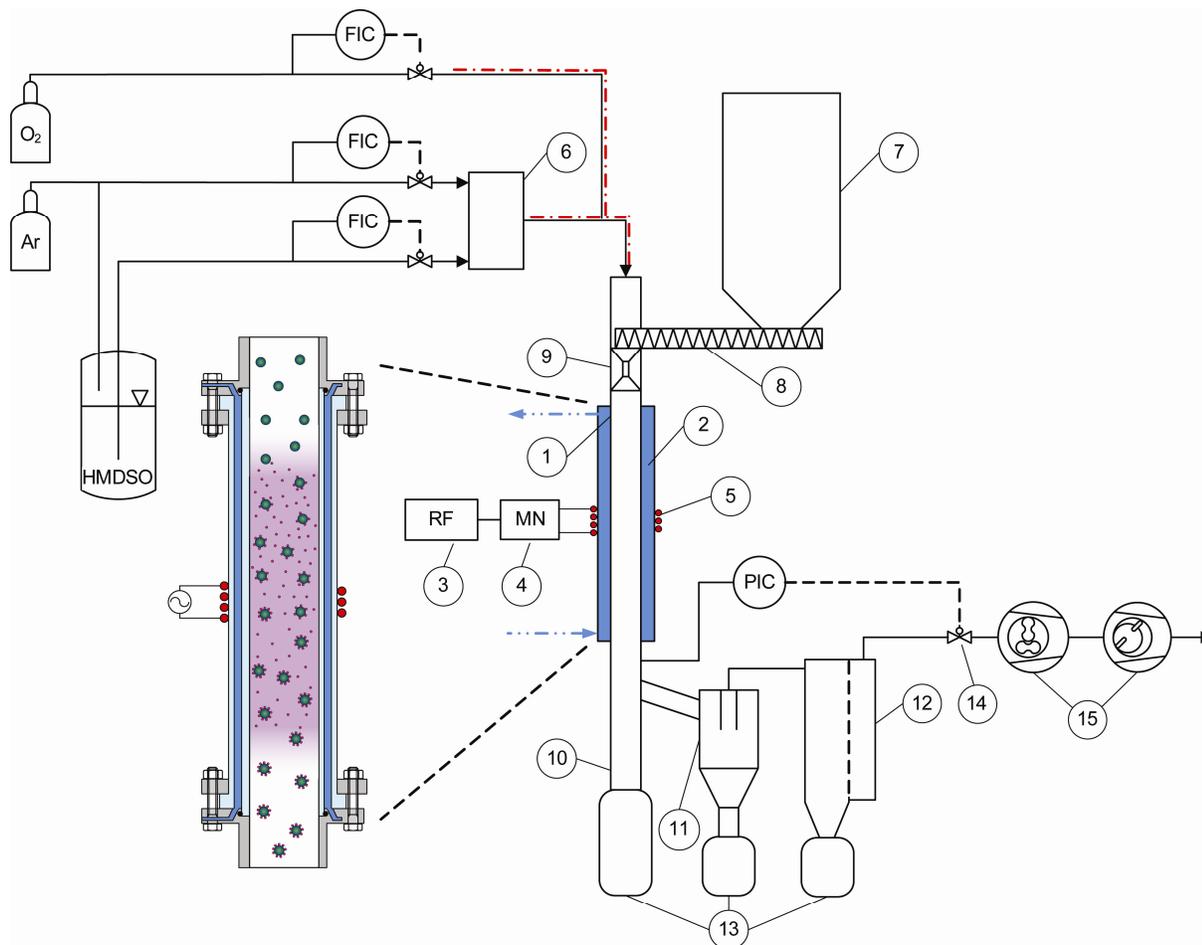


Figure 1: Process scheme of the plasma downstream reactor and principal sketch of the plasma chamber.

efficiency grade 99.94 % for particles between 0.2 and 2 μm , Tecnofil, Switzerland) before and after the nanoparticle production.

2.3 Organosilicon Monomers

For this study two organosilicon monomers, hexamethyldisiloxane (HMDSO) and tetraethyl orthosilicate (TEOS), are compared. The chemical structure of both monomers is shown in Figure 2. HMDSO contains two silicon atoms bonded to one central oxygen atom, each saturated with three methyl groups. TEOS consists of only one central silicon atom which is surrounded by four oxygen atoms, saturated each by an ethyl group.

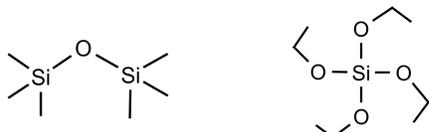


Figure 2: Organosilicon monomers HMDSO (left) and TEOS (right).

2.4 Flowability

The flow behavior of the lactose powder is characterized by the flow factor ff_c , which is defined as the ratio

between the consolidation stress σ_1 and the unconfined yield strength σ_c .

$$ff_c = \frac{\sigma_1}{\sigma_c} \quad (2.1)$$

The flow behavior is classified according to [4] as not flowing for $ff_c < 1$, very cohesive for $1 < ff_c < 2$, cohesive for $2 < ff_c < 4$, easy flowing for $4 < ff_c < 10$ and as free-flowing for $10 < ff_c$.

The flow factor is measured with a ring shear tester (RST-XS, Schulze Schüttguttechnik, Germany) and a shear cell volume of 30 ml. The preshear stress is set to 5000 Pa and shear stresses of 1000, 2500 and 4000 Pa are applied to determine the yield locus and thus, the flow factor.

2.5 Chemical Analysis using XPS

The surface chemistry of selected powders was investigated with x-ray photoelectron spectroscopy (XPS) using a Kratos Axis Nova spectrometer (Kratos Analytical, Manchester, UK). A layer (between 0.5 and 1 mm thick) of the powder was fixed with double sided carbon tape on the sample holder. The samples were illuminated with monochromatic $\text{AlK}\alpha$ irradiation, run at 225 W (15 kV, 15 mA).

The photoelectrons were analyzed with a hemispherical analyzer, operated in the fixed analyzer-transmission mode with a pass energy of 40 eV.

A charging of the powder was over-compensated with slow electrons from the neutralizer. The spectrometer was calibrated according to ISO 15472:2010 with an accuracy better than ± 0.05 eV.

Peak shifting was corrected by referencing aliphatic carbon to 285.0 eV [5]. The peak fitting was performed after subtraction of an iterated Shirley background [6]. The quantitative composition was calculated by correcting the peak areas by the transmission function and the sensitivity factors given by Kratos assuming a homogeneous compound.

3 RESULTS

The standard operating conditions and the investigated parameter range for the presented plasma process are summarized in table 1.

Parameter	Standard	Variation
Plasma Power	300 W	200 - 350 W
Pressure	200 Pa	200 - 400 Pa
Argon flow rate	950 sccm	475 - 1425 sccm
Oxygen flow rate	500 sccm	250 - 750 sccm
Monomer flow rate	50 sccm	25 - 100 sccm

Table 1: standard process parameters and its variation.

Depending on the process conditions the amount of generated nanoparticles, their size and chemistry can be influenced resulting in different flow factors and wetting properties of the treated substrate powder.

The chemical composition (measured by XPS) of the pure nanoparticles derived at standard process conditions (see Table 1) is shown in Figure 3 for both monomers HMDSO and TEOS.

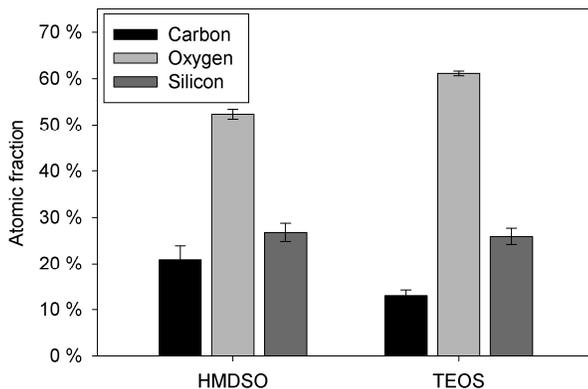


Figure 3: Chemical composition of nanoparticles derived from HMDSO and TEOS at standard operation conditions.

Entering the discharge the monomer molecule disintegrates into smaller fragments, radicals and ions. Nanoparticles nucleate from free radicals and many of the hydrocarbon tails react to stable volatile molecules such as CO_2 or

H_2O . In general particles with the composition $\text{Si}_x\text{O}_y\text{C}_z$ are formed, while the carbon content is much lower for the particles from TEOS, since the silicon atom has already four oxygen bonds in the monomer. During the nucleation of particles from the monomer HMDSO more Si-C bonds remain and are therefore also found in the product.

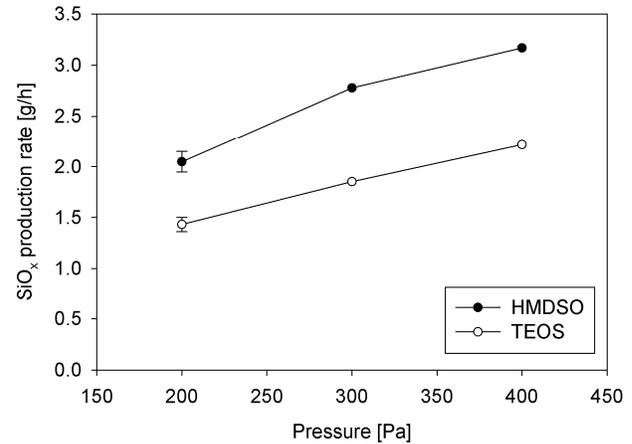


Figure 4: SiO_x production rate as a function of the system pressure (plasma power: 300 W, flow rates: 50 sccm monomer, 500 sccm O_2 , 950 sccm Ar).

In Figure 4 the production rate of nanoparticles is shown as a function of the system pressure. As reported in other reactor systems, more nanoparticles are formed at elevated pressures [7]. The maximal theoretical production rate from monomer to stoichiometric SiO_2 calculates to 16.06 g/h for HMDSO and 8.03 g/h for TEOS respectively, since HMDSO has two silicon atoms per molecule. Thus, the higher mass production rates with the monomer HMDSO compared to TEOS at the same process conditions can be understood. On the other hand the plasma-assisted conversion from monomer to nanoparticles is higher for TEOS (17.8 - 27.8 %) compared to HMDSO (12.8 - 19.7 %).

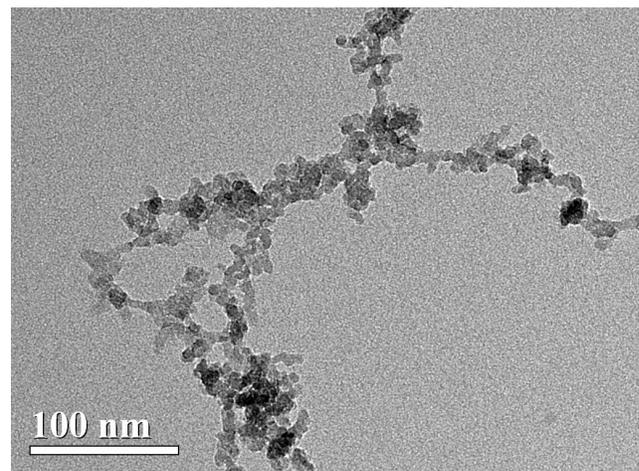


Figure 5: TEM image of agglomerated nanoparticles produced from HMDSO at 300 Pa (plasma power: 300 W, flow rates: 50 sccm monomer, 500 sccm O_2 , 950 sccm Ar).

In Figure 5 a TEM image of a typical nanostructure is shown. The evolving nanoparticles with primary particle sizes below 10 nm are aggregated to larger structures, due to the absence of any substrate material, where the nanoparticles are normally deposited.

Based on a comparison of TEM micrographs and the measurement of the mass production rate at different pressures, it can be concluded that the primary particle size slightly decreases and the mass increases for rising pressure.

If any substrate material is added to the reactor, the SiO_x nanoparticles are directly deposited on the surface of the dispersed substrate powder and lead to macroscopic changes of the powder properties.

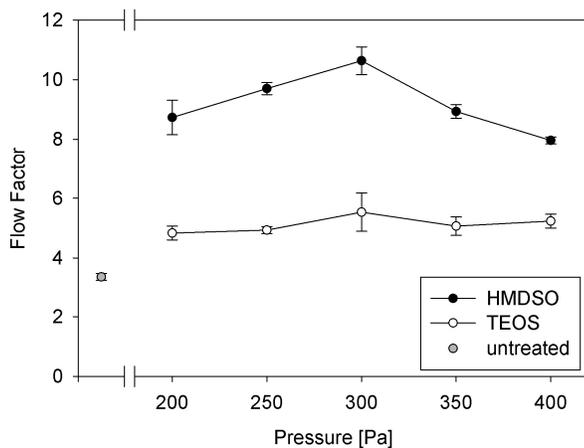


Figure 6: Flow factor as a function of the system pressure (plasma power: 300 W, flow rates: 50 sccm monomer, 500 sccm O₂, 950 sccm Ar).

The flow factor of the investigated substrate material lactose with a median particle diameter of 30 μm is 3.4 and the powder thus classified as cohesive. If the powder surface is covered with SiO_x nanoparticles in the PDR the flow factor can be increased to values which are classified as easy or even free flowing, as illustrated in Figure 6. A maximal flow factor is reached for HMDSO at a process pressure of 300 Pa. The amount and size of deposited nanoparticles at this process conditions builds up a surface roughness, where a maximal reduction of interparticle forces is reached.

In general higher flow factors are measured if the nanostructures are formed from the monomer HMDSO compared to TEOS. This large difference can not only be attributed to the higher nanoparticle production rate with HMDSO and the therewith reached higher surface roughness. Powders processed with HMDSO feature a surface with a lower surface free energy. The depositions originating from TEOS show more polar groups which contribute to the attractive interparticle forces and therefore compensate a part of the improved flow behavior.

As a consequence the powders covered with particles from TEOS dissolve much faster in water than powders

with are covered with HMDSO derived particles but reach lower flow factors.

4 CONCLUSION

SiO_x like nanoparticles are deposited on the surface of much larger lactose particles in a plasma downstream reactor and a residence time of around 0.1 s. The deposited structures lead to a reduction of the interparticle forces and thus improve the powder flow behavior. The flowability improvement is higher if the nanostructures emerge from the monomer HMDSO, where the depositions are hydrophobic, compared to particles emerging from TEOS which have a higher surface free energy. As an example the influence of the process pressure on the nanoparticle production and thereby achieved flowability improvements is shown.

If the complex interplay between plasma parameters, nanoparticle nucleation and deposition on substrate materials is better understood, macroscopic powder properties like the wettability or flowability can be tailored by only slight variations of the process conditions. This could open up new application fields of this technology in many powder processing industries.

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