COATING OF FINE AEROGEL PARTICLES USING SPOUTED BED TECHNOLOGY

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Abstract–Aerogels are porous and light-weighting materials with high inner surface area. Their properties enable to use them in many fields, e.g. as acoustic and thermal insulation materials, catalyst, adsorber or drug carriers. However, open pore structure does not allow their application in different areas because of change of the structure caused by liquid-contact. Therefore there is a protective layer on their surface needed, which provides new fields of application, e.g. in food products. In this work coating of the protein-based aerogel microspheres ($d_P < 100$ µm) with shellac using spouted bed technology was performed. This method enables applying of dense, uniform and thin coating layer on fine particles. To improve the uniformity of the coating layer the specific surface area before and after the coating procedure was measured and showed clear decrease after longest coating time. To investigate the behavior ofaerogels in water containing medias the particles were exposed to water drops using sessile drop protocol. The coating protects the aerogel particles from water influence.

INTRODUCTION

Aerogels are a group of very light materials made from gels, in which the liquid component is replaced by the gas in a supercritical drying process (Garcia-Gonzalez et al., 2012). Resulting microporous network with open pore structure enables application of aerogels as acoustic and thermal insulation materials, catalyst, adsorber, drug carriers and when derived from edible materials also as functional food (Alnaief et al., 2012). Open pore network allows on the one hand high loading capacity of an active ingredient; on the other hand it leads to penetration of liquids into the material causing change of its structure (Alnaief et al., 2012). This makes the storage of the aerogels in water containing food products impossible. Applying an additional coating layer on the surface of aerogels opens new opportunities for food industry as well as their application in many other fields.

A possibility to coat very fine particles is given by spouted bed technology (Salikov et al., 2015). This method is frequently used for industrial processes like spray granulation, coating or drying of particles, when intensive contacting of gas and solid particles is required (Gryczka et al., 2009). In comparison to conventional fluidized bed, the gas is introduced into the process chamber by one or more slits instead of the porous gas distribution plate and thereby handling of coarse, irregularly shaped or fine particles is possible (Gryczka et al., 2007). Due to the simple construction a characteristic and uniform particle circulation is achieved (see Figure 1).

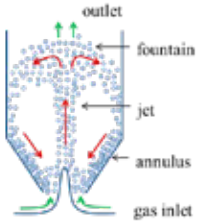

Figure 1: Scheme of the particle circulation in a prismatic spouted bed with two gas inlet slits.

The particles placed in the process chamber are entrained by a jet with high gas velocities to the top of the apparatus where a fountain is formed. The particles reach then the annulus zone and slide back downwards due to the gravity to the process chamber and are entrained by the gas again (Epstein, 2011). For processing of such fine particles as aerogel microspheres stable spouting operating conditions can be achieved when particles are highly dispersed in the apparatus at high gas velocities (in so called dilute spouting regime)(Salikov et al., 2015). When coating solution droplets are introduced into system at these high bed porosities the evaporation of the solventis faster due to intensive heat and mass transfer and takes place before the solvent penetrates into the pore network inhibiting structural changes of particles.

In this work a coating process of protein-based aerogels with different amounts of shellac solution in a novel prismatic spouted bed is proposed. To improve the stability of the coating in water containing medias, the untreated and coated particles were exposed to water droplets using the sessile drop protocol.

MATERIALS AND METHODS

Aerogels

As a bed material already existing whey protein isolate (WPI) aerogels were used. The preparation process of these aerogel-microspheres can be found in (Betz et al., 2012). For this study aerogel microspheres were produced at following conditions: pH = 7 of the gel, gelation at 80 °C, supercritical carbon dioxide drying at 120 bar and 40 °C for 8 h. The particles are characterized by the BET surface area of 98 m^2/g with the pore volume of 0.21 cm^3/g.

Coating solution

As a coating material 20 wt.-% shellac (SSB Pharma 56 Flakes, HARKE Pharma GmbH, Germany) solution in ethanol (≥99.8% with ca. 1 % MEK,Carl Roth GmbH, Germany) was used. To monitor the progress of coating procedure shellac solution was dyed with patent blue (Ruth GmbH & Co. KG, Germany).

Coating in spouted bed

Coating of the aerogel microspheres was performed in a in-house built spouted bed apparatus (see Figure 2). This experimental plant consists of a prismatic process chamber with two horizontal gas inlets, a conical expansion zone and a cylindrical relaxation zone. For the observation of the flow behavior two plexiglass plates were placed in the front and back sides of the process chamber. The fluidization air enters the process chamber from the bottom through two slots. The velocity of the gas can be adjusted by changing the height of these slots. The gas inlet flow rate was chosen to 4 m^3/h and increased up to 17 m^3/h during coating of 80 g of particles. The temperature in the process chamber was adjusted to 30 °C. For the spraying of the coating solution a 2 mm two-fluid-nozzle was placed in the middle of the process chamber. Spraying of shellac solution with pressured air (1 bar) occurred in the direction of the gas flow in so called bottom-spray configuration. The coating solution was heated up to 35 °C and then sprayed using syringe pump with the flow rate of 0.5 ml/min. This very low spraying rate was chosen to avoid bed collapse during coating due to a too high amount of the liquid in the process chamber and in order to reduce additional drying time of the bed during operation. Particles were coated up to 340 min.

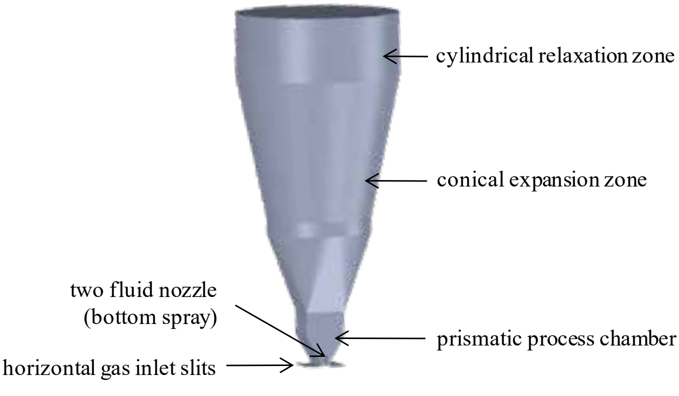

Figure 2: 3D scheme of the spouted bed apparatus.

Particles characteristics

The untreated and coated aerogel microspheres were characterized using different analytical methods to evaluate the quality and thickness of the coating layer. Particle size distribution was measured using dynamic image analysis with CAMSIZER XT (Retsch GmbH, Germany). BET surface area and pore size were measured using low temperature nitrogen adsorption (Nova 3000e Surface Area Analyzer, Quantachrome Instruments, USA). Before analysis the samples were degassed under vacuum conditions for 20 hat 40 °C. Images of the particles were made using scanning electron microscopy Leo Gemini 1530 (LEO Elektronenmikroskopie GmbH, Germany) at 2 kV. Before imaging the samples were sputtered with 7 nm gold layer to avoid charging.

Coating layer thickness

The layer thickness of a particle was determined by slicing using FIB instrument (FIB FEI Strata 205, USA). To create the cross section of the single coated particle a focused beam of gallium ions with high current of 7 nA was used. To make the cross section and the coating layer visible polishing with lower currents of 3 nA, 1 nA, 0.5 nA and 0.1 nA consecutively was performed (Giannuzzi, 2005).

Stability of the particles

To improve the stability of the coated particles during storage in water-containing media aerogel particles were pressed into tablets and then exposed to 2 µl water droplets at room temperature using sessile drop protocol described in detail here (Reinke et al., 2015, see also Figure 3). Images of the droplet deposited with precision syringe (Multipette, Eppendorf AG, Germany) were recorded with a high-speed camera (Series NX-S2) using a microscope objective (OPTEM ZOOM 125) at a frequency of 100 Hz. The setup was equipped with the software Motion Studio (Integrated Design Tools Ltd., USA). The LBDSA drop shape plug-in in ImageJ was used to analyze the images. Tablet pressing was carried out with Texture Analyzer (Stable Micro Systems, UK), where a force of 100 N at stressing velocity of 0.05 mm/s was applied. Additionally, the apparent contact angle (see Figure 3) of water for five measurements was calculated. Apparent contact angle represents the angle on a rough surface between the baseline of the apparent solid surface and the tangent on the droplet surface curvature (Reinke et al., 2015). Due to imperfections of the surface and heterogeneity of the sample it differs from the intrinsic contact angle according to the Young's Equation (Young, 1805). That is based on the force balance between the surface energies of liquid and solid with gaseous phase (σ_{lg}, σ_{sg}) and interfacial tension between solid and liquid phases (σ_{ls}, see Eq.(1)) and gives information about the energy state of a solid material. If a liquid wets the solid material there is a contact angle of less than 90 °. Contact angle larger than 90 ° corresponds to non-wetting liquid (Yuan et al., 2013).

$$\cos\theta = \frac{\sigma_{sg} - \sigma_{sl}}{\sigma_{lg}} \tag{1}$$

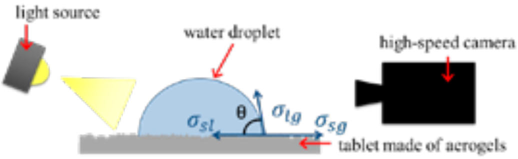

Figure 3: Scheme of the sessile drop protocol with force balance between the surface energies.

RESULTS AND DISCUSSION

Particles characteristics

Figure 4 shows SEM images of WPI microspheres before and after coating. Untreated particles are in form of single particles having smooth and porous surface. Coated particles are characterized by rough surface, which indicates the presence of the coating on the particles. On their surface single spreaded shellac droplets are visible, which are partially covered with very fine particles or particles parts and solidified shellac droplets. Besides of sticking of fine parts to the aerogel surface also agglomerates consisting of more particles are present. Figure 5 shows particle size distribution (PSD) of untreated and coated WPI-aerogels with three different amounts of shellac solution (80, 131 and 170 ml, corresponding to 160, 262 and 340 min of coating). Table 1 gives an overview of mean particle characteristics and specific surface areas determined using BET method. The values lower than 20 m^2/g are based on the limitation of the measuring device.

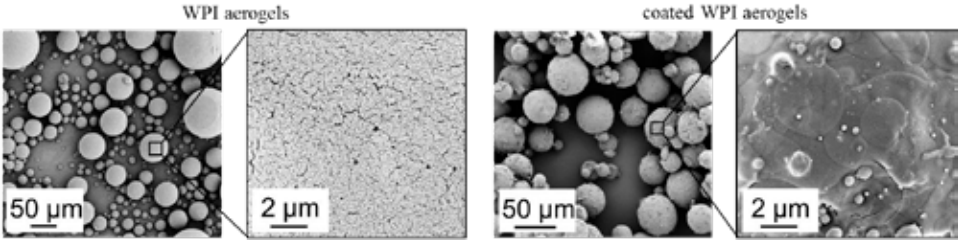

Figure 4: SEM images of whey protein isolate aerogel particles before (left) and after (right) coating.

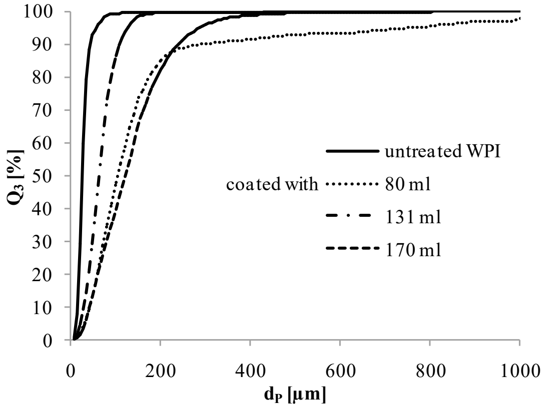

Figure 5: Cumulative particle size distribution of the WPI-aerogels before and after coating with 80 ml, 131 ml and 170 ml of shellac solution.

Figure 5 shows in case of spraying of 80 ml and 170 ml of the shellac solution clearly a broader particle size distribution compared to the 131 ml curve, which is due to formation of agglomerates during coating. All experiments were carried out at the same process parameters and only additional drying intervals with different duration were introduced, e.g. when changing the syringe in the syringe pump or if the bed was to wet and tended to collapse. During additional drying intervals the applied shellac layer solidifies and the amount of liquid bridges between particles can be lower, so that a lower amount of agglomerates is present. Therefore, there is a need to investigate the influence of the duration of additional drying steps during coating on the generation of agglomerates and variation of the nozzle pressure to find optimal parameters to avoid sticking of the particles.

Table 1: Overview of mean particle diameters and specific surface area for untreated and coated aerogels.

Particle characteristics	untreated WPI aerogels	WPI coated with 80 ml of shellac solution	WPI coated with 131 ml of shellac solution	WPI coated with 170 ml of shellac solution
diameters [µm]				
$d_{10,3}$	14.3	40.8	27.5	40.7
$d_{50,3}$	24.5	103.8	62.2	120.6
$d_{90,3}$	41.0	288.3	107.9	238.2
BET surface S_{BET}[m^2/g]	98	< 20	42	< 20

When comparing the results for analysis of the surface area (see Figure 5), the coating with the lowest and highest amount of shellac solution leads to decrease of the surface area up to 80 %, which indicates good coating quality. In case of coating with 131 ml the uncovered surface is much larger - only 43 % of the surface is covered by shellac. These results correspond to PSD showed in Figure 5, because due to agglomeration the pores of the particles are not available for nitrogen adsorption leading to lower values of BET surface area. In case of particles coated with 131 ml of the solution the particles are not strongly agglomerated and also not coated uniformly, so that the BET value is much higher.

Layer thickness

Figure 6 shows the SEM image of FIB cross-sectioning of a representive WPI-aerogel particle inclined to 45 °. There is clearly a coating layer on surface of the particle visible. Underneath the coating layer the slicing pattern of FIB instrument is present. The removed parts of the particle during operation are left in its front. The coating layer is uniformly distributed over the particle as expected. The thickness of the shellac layer is 1.172 µm high and 1.582 µm wide in the thickest point. Since only the layer thickness after spraying of 60 ml was measured the influence of spraying time on the thickness has to be investigated.

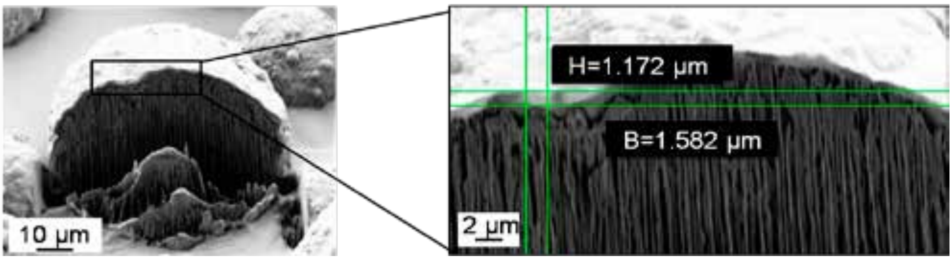

Figure 6: SEM of FIB cross sectioning of a representative coated WPI aerogel-particle after coating with 60 ml of coating solution.

Sessile water drop on aerogel tablet surface

Figure 7 left shows the change of the size and shape of water droplet on the surface of tablets of uncoated and coated (170 ml of shellac solution) WPI aerogels with increasing time up to 60 s. For untreated particles the decrease of the drop volume takes place immediately after the deposition. Water penetrates to the pores of single particles and causes swelling on the top of the tablet, which can be seen in the top of Figure 7 right. In case of the coated tablet, the surface is unaffected at the beginning and the drop volume decreases only after a long period of time. There is also nearly no swelling on the top of the sample (see Figure 7 right, in the bottom). This happen because water penetrates into the porosity of the tablet and not that one of single particles, which indicates that coated aerogel-particles are more stable when exposed to water contact compared to untreated ones. Therefore, we can conclude that coating protects the particles from water.

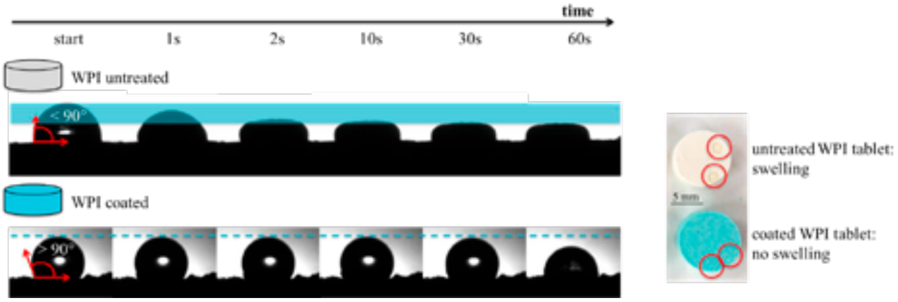

Figure 7: Left: Change of the size and shape of water droplet deposited of the surface of tablets pressed of untreated and coated whey protein isolate aerogels with increasing time. On the first image the apparent contact angle of water on respective material is marked. Right: Surface of both tablets after water drop deposition. Circles indicate the areas of water drop contact.

Table 2 gives an overview on the apparent water contact angles on the samples with uncoated and coated aerogel particles. The contact angle measured directly after deposition is measured to 84.67 °, which corresponds to wetting of water on aerogels. In case of the treating the particles with a hydrophobic material as shellac (PhanThe, 2008) the average contact angle for coated particles is 114.45 °, which indicates non-wetting behaviour. Since the contact angle is dependent on the roughness of the surface (Reinke et al., 2015) and the roughness of both tablets is different (see Figure 7) next step in the ongoing research is the investigation of this phenomena.

Table 2: Water contact angle ontablets made from uncoated and coated aerogels.

Sample	Water contact angle [°]
untreated WPI	84.67 ± 7.65
coated WPI	114.45 ± 9.90

CONCLUSION

In this work protein-based aerogels were successfully coated in a prismatic spouted bed apparatus with different amounts of coating solution. A decrease of specific surface area after coating procedure was observed. To minimize the generation of agglomerates the influence of the duration of additional drying intervals (intermittent coating operation) should be investigated. The layer thickness was successfully measured using FIB cross-sectioning method. The apparent contact angle of coated particles is higher than for untreated ones. In further investigations the influence of the surface roughness of the samples should be measured. It was showed that coating has a protective function against water penetration, so that the coated particles can be used in application fields like water containing food products.

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NOTATION

θ	contact angle , °	σ_{sg}	solid/gas surface energy, N/m
σ_{lg}	liquid/gas surface energy, N/m	σ_{sl}	solid/liquid surface energy, N/m

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