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Article

Biopolymer-based Aerogel Bead Production via Jet Cutting Method

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Abstract: The aim of this work is to develop a method to produce spherical biopolymer-based aerogel particles, which is capable for scale up in the future. Therefore, jet cutting method is suggested. Amidated pectin and sodium alginate were used as precursor (1-3 wt.-% solution) for particle production via jet cutting. Gelation was realized via two methods: internal setting method (using calcium carbonate particles as cross-linker and citric and acidic acid for pH adjustment) and diffusion method (in calcium chloride solutions). Gel particles were subjected to solvent exchange to ethanol and consequent supercritical drying with CO_2. Spherical aerogel particles with narrow particle size distribution in the range of 400 to 1500 µm and with specific surface area of around 500 m^2/g could be produced. Overall, it can be concluded that jet cutting method is suitable for aerogel particle production, although the shape of the particles is not perfectly spherical in all cases. However, parameter adjustment might lead to even better shaped particles in further work. Moreover, the biopolymer-based aerogel particles synthesized in this study were tested as humidity absorber in drying units for home appliances, particularly for dishwashers. It could be shown that for several cycles of absorption and desorption of humidity aerogel particles are stable with an absorption capacity of around 20 wt.-%.

Keywords: aerogel; biopolymer; pectin; alginate; chitosan; beads; jet cutting

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1. Introduction

Biopolymer-based aerogels get more and more important for different applications in foods, pharmaceuticals, tissue engineering, catalysis, and cosmetics in the last decades [1],[2],[3],[4],[5]. In many of these applications round shaped particles and beads with narrow particle size distribution are advantageous for handling, processing, and application requirements. For instance for pulmonary drug delivery small particles (below 10 microns for porous aerogel particles)[6] are required to enable the drug transport to the lung. Thereby spherical shape of the particles is required for a good flowability. In food industry hydrogel particles can be used to mimic the taste and mouth feel of fat emulsions with reduced fat content [7]. In many applications millimeter-sized spherical aerogel beads are used in catalysis [8].

To produce aerogel particles or beads of different sizes diverse methods can be used, most promising being dripping and emulsion gelation method. In emulsion gelation method the aqueous biopolymer solution is dispersed in an oil phase. Resulting emulsions are stabilized by using surfactants. Subsequently, gelation of the droplets (dispersed phase of the emulsion) is induced by addition of a solution of the gelling agent [9]. Principally, the scale up of the emulsion gelation method for production of large amounts of aerogel particles is possible. One way could be a scale up of the stirred vessel size for the production of biopolymer solution emulsion. Another possibility is the continuous production of emulsions (for instance by a rotor-stator machine). After the gelation process, gel particles have to be separated from the continuous oil phase and dried to be converted into aerogel particles.

Particle sizes of few hundred microns up to several millimeters can be achieved with different variations of the dripping method like simple dropping and vibrated dropping [10]. Within the dripping method biopolymer solutions are dropped into a gelation bath where a gelling agent induces gelation[5]. Particle size depends mainly on the tube or nozzle diameter used [10]. Dripping method delivers particles with narrow particle size distributions, but is quite work intensive and enables only limited throughput. Further, all dripping methods are limited by the viscosity of processed solutions. Thus, a scale up of the dripping method could rather be realized via multiplication of the number of nozzles than via scale up of the whole process and apparatus [10].

So far, the production of biopolymer aerogel particles have been realized only as a batch processes on a small scale, no scale up approaches were demonstrated.

However, to enable industrial applications a new and scalable production technology for aerogel particles is required. Whereas for the production of small aerogel particles (below 500 µm) emulsion-gelation method described above seems to be promising [2],[11] for larger particles an alternative enabling the high throughput (or continuous) production is needed. In this work we suggest the jet cutting method for the production of biopolymer-based aerogel particles and beads as an alternative to dripping techniques.

Throughout the jet cutting method a liquid jet of biopolymer solution is cut by a rotating cutting disc. Obtained liquid cylinders fall along their trajectory to the ground. Throughout falling, due to surface tension cylinders form spheres. At the end of the particle trajectory liquid drops are collected. So far, the jet cutting method is used for the production of inorganic and organic spherical beads for diverse pharmaceutical, agricultural, cosmetic and cleaning applications [10] (https://www.genialab.com/production/). Particle sizes can be set between few hundred µm and up to several mm with different parameters like nozzle diameter, jet velocity, cylinder ratio and cutting frequency[10]. Two scale up methods for the jet cutting method are possible: (1) multiplication of the number of nozzles, although this method show drawbacks related to increased cutting loss, and (2) increase of cutting frequency to increase the number of produced particles. For the increase of cutting frequency several parameters like throughput, jet velocity and cutting velocity have to be adjusted at the same time to maintain particle size and shape[10]. The jet cutting method overcomes the limitation of simple dripping methods regarding the viscosity limitation of processed solutions [10],[12]. Adjustment of the jet cutting process can also enable processing of low viscous solutions [12]. Production of alginate beads via jet cutting method has been shown before [12],[13], however they were not converted into aerogels.

At the end of the particle trajectory droplets are gelled. Gelation of biopolymer solutions can be achieved with different gelation methods, most suitable for the jet cutting process being “bath-gelled” methods like acid induced gelation or ionotropic gelation [14], [15]. When biopolymer solutions come into contact with the gelation bath admixed cross-linker or acids in the bath liquid, gelation progresses from the outside of biopolymer solution drops to their center. Thereby two general methods can be identified: (1) diffusion method and (2) internal setting method [1]. In the diffusion method the gelation inducing agent (e.g. ions or acid) diffuses from the gelation bath into the biopolymer solution, inducing the gel formation from the outer layer of the droplet towards its core. Thereby the gelation rate is mainly controlled by the diffusion. For the internal setting method the solid gelling agent is dispersed inside the biopolymer solution and gelation is triggered by the subsequent dissolution of the agent due to changes of external conditions like pH value or temperature [1]. Due to this, gelation occurs more homogeneously throughout the droplet.

In this work both gelation methods are combined with the jet cutting in order to produce biopolymer-based aerogel particles from alginate and amidated pectin, respectively. The jet cutting method is adjusted to perform the gelation process directly in the collecting bath at the end of the droplet trajectory, thereby the conditions allowing to avoid agglomeration of particles are identified. Strategies to perform the subsequent solvent exchange and the supercritical drying of the particles are discussed.

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After the production of biopolymer-based aerogel particles, it was aimed to test the aerogel materials as humidity absorber in drying units for home appliances, particularly for dishwashers. Throughout the whole washing cycle of a regular dishwasher, the drying step itself consumes a considerable amount of total energy of about 45% of the overall energy consumption by heating up the water temperature to approximately 65°C. It is possible to reduce the energy consumption by more than 20% by lowering the heating temperature or even eliminating the heating step from the drying cycle by using water vapour absorbers. The prove of usability of biopolymer-based aerogels for the application of water vapour absorbers will show the potential of aerogels to not only reduce the energy consumption significantly but it will also be the first usage of aerogels in this kind of application in the market. The outcomes of this study will help to widespread the usage of aerogels in other appliances such as driers, refrigerators, or even in products of electronic industry where humidity is an important concern towards the goal of corrosion prevention.

2. Materials and Methods

2.1 Materials

Amidated pectin (29% of esterification (DE), 21% of amidation (DA)) was kindly provided by Herbstreith und Fox KG, Germany. Calcium carbonate ($CaCO_3$, light, precipitated powder, $D_{50} = 1\ \mu m$) was kindly provided by Magnesia GmbH, Germany. Sodium hydroxide (NaOH), citric acid, and calcium chloride ($CaCl_2$) were purchased from Th. Geyer GmbH & Co.KG, Germany. Denatured ethanol 99.8%, and pure ethanol 99,5% were obtained from Carl Roth GmbH & Co. KG and carbon dioxide (CO_2) with a purity of 99.9% was supplied by AGA Gas GmbH, Germany. Sodium alginate (Hydagen 558P) was provided by BASF, Germany and sodium alginate (BioChemica A3249) was purchased from AppliChem GmbH, Germany. Glacial acetic acid was purchased from VWR Chemical. Shrimp chitosan was purchased from Sigma Aldrich. All chemicals were used as received. Deionized water was used throughout the study.

2.2 Biopolymer stock solutions

Pectin stock solutions were prepared by dissolution of biopolymers in deionized water by using magnetic stirring at room temperature to reach different concentrations (1-3 wt.-%). Part of the pectin solutions is further neutralized with 0.5 M sodium hydroxide to pH 7 and 0.18 g $CaCO_3$/g pectin is added as a cross-linker for internal setting gelation. Solution homogenization was done with a rotor stator machine (IKA magic lab, Germany).

Alginate stock solutions of 1 - 3 wt.-% were prepared by dissolution of alginate powder in deionized water. Stirring was performed with a dissolver stirring tool mounted on a high torque stirrer (Heidolph Hei-Torque 100, Germany). For experiments with internal setting method 0.37 g $CaCO_3$ per 1 g alginate was added and stirred until a homogeneous dispersion was achieved.

Chitosan stock solutions of 3 wt.-% were prepared by dissolution of chitosan in 3 wt.-% acetic acid with mechanical stirring.

2.3 Hydrogel particle production – jet cutting

Hydrogel particles were produced with the JetCutter Typ S from geniaLab GmbH, Germany. The extrusion of biopolymer solution through the nozzle was driven by compressed air from the house supply line. A schematic drawing of the jet cutting process is shown in Figure 1. The throughput was tuned with a pressure-regulating valve. Nozzles with different diameters (250 – 1000 µm) were used to vary particle size. Experiments were carried out utilizing various combinations of nozzles, cutting discs, throughput and cylinder ratios as well as cutting velocities. Two parameters (nozzle diameter and cylinder ratio) were chosen to compare different cutting experiments. Used combinations of these parameters are shown in Table 2.

After cutting, liquid cylinders fell downwards into the collection bath. Throughout falling cylinders form spherical droplets due to the surface tension of the biopolymer solution. A suitable collection bath was placed at a distance of around 50 or 80 cm below the cutting tool. The composition of the gelation bath was adjusted to enable the gelation of the polysaccharide solutions. Used gelation methods and gelation baths for biopolymer solutions are shown in Table 1.

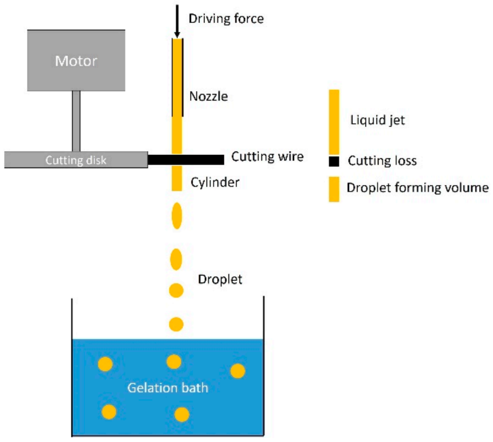

Figure 1: Schematic drawing of the jet cutting process

Table 1: Processed jet cutting experiments

Biopolymer solution	Gelation method	Composition of gelation bath
Sodium alginate (1-3 wt.-%)	Diffusion	Aqueous, 5 g/L $CaCl_2$
Sodium alginate (3 wt.-%)	Internal setting	Aqueous acetic acid (30 wt.-%)
Amidated pectin (2-3 wt.-%)	Diffusion	Aqueous 5 g/L $CaCl_2$
Amidated pectin (1-3 wt.-%), adjusted pH value to 7	Internal setting	Aqueous citric acid (pH 3-4)
Chitosan 3 wt.-%	Diffusion	Aqueous 5% sodium hydroxide

The volume of the gelation bath was at least five times the total volume of the processed biopolymer solution to enable good stirring and particle separation. After finishing the jet cutting, the content of the collection baths was stirred with a magnetic bar for at least ten more minutes to ensure complete gelation of particles and to avoid agglomeration. Gelled particles were removed from gelation bath via filtering. To avoid any loss of particles during collection, filter mesh size below nozzle diameters were chosen. Collected particles were transferred to the solvent exchange.

2.4 Solvent exchange

Two ways of solvent exchange (water to ethanol) were performed on collected particles: 1) direct solvent exchange to 100 wt.-% ethanol, 2) stepwise solvent exchange (30, 60, 90, 100 wt.-% ethanol/ 20, 40, 60, 80, 100 wt.-%) until a final ethanol concentration of 98 wt.-% (respectively 98 vol-%) is reached inside the particles. Further, for some samples an additional washing step with deionized water was performed before starting the solvent exchange to remove remaining components of the gelation bath from the particles and thus to avoid agglomeration during particle collection.

2.5 Supercritical drying

After solvent exchange particles were taken out from the ethanol bath and packed into a filter paper. Supercritical drying with CO_2 was performed in an autoclave at constant temperature of 60°C and pressure of 120 bar. Continuous flow of CO_2 (20 – 80 g/min, respectively 240 g/min) was set until complete extraction of ethanol was done. Afterwards slow depressurization of the autoclave (1-2 bar/min) was performed. Dried particles were collected from the autoclave and stored in sealed boxes until analysis.

2.6 Specific surface area

Specific surface area of aerogel beads were measured via low temperature nitrogen adsorption/desorption (Quantachrome Nova 3000e, Germany and Micromeritics TriStar II 3020, Germany) (BET).

2.7 Scanning electron microscope

Investigation of the inner structure of the resulting aerogels and particle size determination were done via scanning electron microscope (SEM) analysis (Zeiss Supra VP55, Germany). Prior to analysis all samples were sputtered with gold (Baltec Sputter Coater SCD 050).

2.8 Optical microscopy

Shape and size of obtained hydrogel and aerogel particles and beads were examined with an optical microscope (VisiScope TL384H) from VWR, Germany.

2.9 Humidity absorption test

The humidity absorption/desorption capacity of aerogel particles were tested in laboratory scale. For the determination of absorption capacities, aerogel samples were kept in a humidity chamber (Weiss Model, 2017) at two conditions: a) 40°C and 100% relative humidity (RH) and b) 27°C and 80% RH for three hours. Absorption capacity was determined in two ways: a) samples were dried at 60°C over night and the weight of aerogel samples was determined after absorption step and drying step, respectively. The absorption capacity c_{abs} is calculated as ratio between taken up humidity and initial aerogel weight (see Equation 1) b) evaluation of humidity uptake was done with a thermal gravimetric analysis (TGA, TA Instruments Q50). Finally, samples were tested in real prototype dishwashers, were real conditions are simulated. The changing conditions in the dishwasher prototype are shown in Figure 2. Here, the absorption capacity is determined of internal flow and energy consumption measurements of the prototype system.

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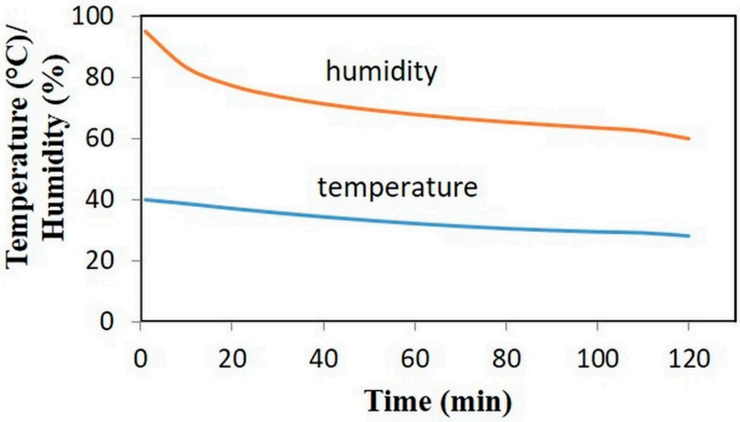

Figure 2: Program set in the humidity chamber simulating the relative humidity and temperature change in the dishwasher during the drying step

The adsorption capacity in percentage is calculated as following:

$$c_{abs} = \frac{w_f - w_i}{w_i} * 100, \qquad (1)$$

where w_i *and* w_f are the initial and final weight before and after adsorption tests.

3. Results and discussion

3.1 Jet cutting method

In this work jet cutting method was combined with two different gelation mechanisms: diffusion and internal setting method (as described in the introduction). For both methods, the gelation in the collecting bath had to be optimized so that the droplets can form a gel without agglomeration or coalescence with other droplets/particles. Therefore, one of the most crucial parameters of the process is the gelation time.

High gelation rate might lead to an immediate gelation after the first contact of solution droplets with the gelation bath. Additionally, a low surface tension of the droplets might cause strong deformation during their hit on the gelation bath surface. Both factors might lead to a situation, when the droplet deformed by the hit on the surface of the bath`s liquid is "frozen" immediately by fast gelation. On the other hand, inappropriately long gelation times might cause deformation of liquid droplets or their coalescence during stirring in the gelation bath, thus leading to a non-uniform particle size and shape. Depending on the polymer type, slow gelation rates might cause in-proper gelation after set gelation times. That would result in the collection of only partly gelled particles what might lead to a dissolution of non-gelled drops during the washing step before solvent exchange. Therefore, the effects of the pH value of the solution, temperature, viscosity, and biopolymer concentration on the gelation rate should be accounted to understand their impact on the resulting particle shape. Another important parameter influencing the particle shape is the distance between the cutting tool and the collection bath, which needs to be properly adjusted.

In this work all studied biopolymer solutions were processed with a table top sized JetCutter. The flow was induced by pressurized air. Pressures between 1 and 2 bar were sufficient to reach throughputs between 2 and 13 kg/h. Among others, two important parameters of the jet cutting process are the cylinder ratio, which describes the ratio between the height and the diameter of the cut cylinders and the nozzle

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diameter which influences directly the jet diameter. The optimum values of these parameters for the production of spherical particles of certain size depend on the solution properties, like viscosity and surface tension. Nevertheless, both parameters are not the only ones influencing the particle shape and size during the cutting process; the nozzle diameter is important to set the cylinder diameter, and therefore, strongly influences the particle size as well.

Thus, one of the goals of this work was to find the optimal cylinder ratio in combination with the nozzle diameter, which lead to perfect sphericity of the particles and narrow particle size distribution.

Table 2: Nozzle/cylinder ratios used for jet cutting of different biopolymer solutions

Solution	Nozzle diameter [µm] / cylinder ratio				
Pure pectin in $CaCl_2$, diffusion method	250/8.9	350/2.5-5.2	450/0.7-9.1	500/1.8-12.1	1000/0.6-2.1
Pectin/ $CaCO_3$-, acid induced internal setting	n.a.	n.a.	450/1.2-11.6	500/0.9-9.6	n.a.
Pure alginate in $CaCl_2$, diffusion method	n.a.	300/10.1	400/9.8	500/12.4	600/9.6
Alginate/$CaCO_3$-, acid induced internal setting	n.a.	300/8.7	n.a.	500/9.4	900/8.5

Different cylinder ratios (cylinder height/cylinder diameter) were realized by tuning the nozzle diameter (from 250 to 1000 µm), the throughput and the cutting frequency as shown in Table 2. Thereby, jet velocities were calculated to be between 3.3 and 12 m/s according to nozzle/throughput combinations used. Cutting of the jet causes a loss of biopolymer solution (a volume with height equal to the cutting wire diameter), as shown in Figure 1. This loss is accelerated in a vertical direction to the jet and collected in the so called shield to avoid distribution. The cutting efficiency is determined from the amount of solution lost in the shield and depends on cutting frequency, jet velocity, and cutting angle. Experiments with small nozzle diameters below 500 µm often resulted in blocking of the nozzle. The same was observed for the high biopolymer concentrations (3 wt.-%) due to high viscosity and possible pre-gelation inside the jet cutting system. Stable jets of homogeneous flow and constant velocity and, therefore, constant volume flow could be obtained only from homogeneous solutions. Otherwise, inhomogeneity of viscosity or flowability resulted in moving jets of varying diameters and therefore, non-constant cylinder properties.

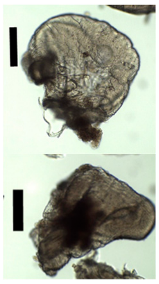
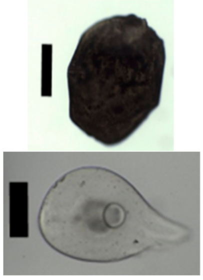
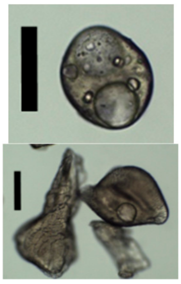
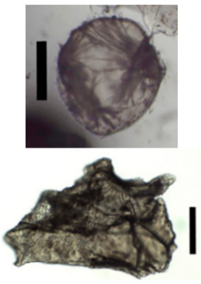
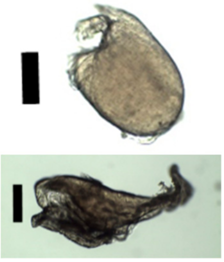
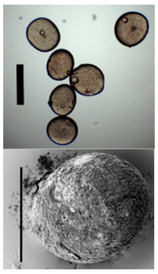
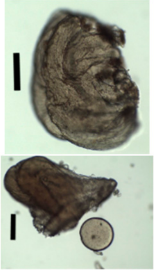
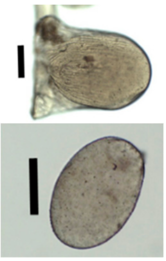
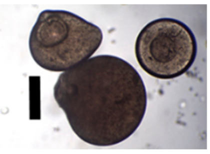
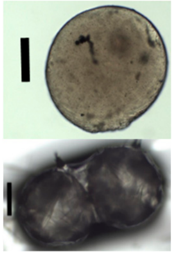
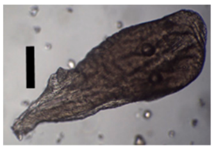
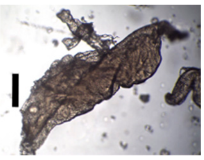
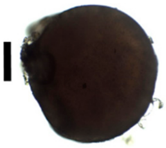
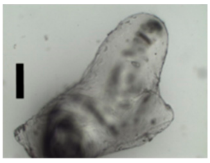
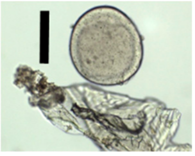
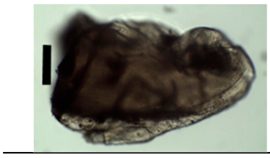
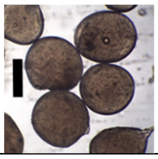
3.2 Diffusion method

The diffusion method of gelation could be applied to both aqueous solutions of pure pectin and pure alginate (2-3 and 1-3 wt.-%, respectively).

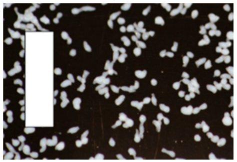
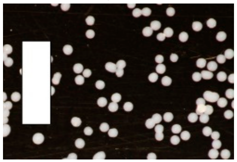
Solutions of both biopolymers with different concentrations were jet cut and collected in a gelation bath containing aqueous 0.5 wt.-% $CaCl_2$ solution. Even though the particles shape within one batch was not quite homogeneous, almost spherically shaped beads could be observed for all combinations of nozzle diameter and cylinder ratio. Obtained particles are shown in Table 3.

Table 3: Used combinations of nozzle diameters and cylinder ratios for the production of gel particles via diffusion method

Gel particles obtained from 3 wt.-% amidated pectin solution by diffusion method (nozzle diameter/cylinder ratio, black bar corresponds to 200 µm, * 2 wt.-% amidated pectin)

250/8.9	350/2.5	350/2.6	350/4.3
			
350/5.2	450/0.7	450/1.7	450/4.2
			
450/9.1	500/1.3	500/1.8	500/2.2
			
500/3.5	500/6.0	500/12.1	1000/0.6
			
1000/2.1	*450/1.5		
			

Gel particles obtained from sodium alginate solution by diffusion method (nozzle diameter/cylinder ratio, alginate concentration, white bar corresponds to 5 mm)

300/10.1, 1 wt.-%	400/9.8, 2 wt.-%	500/12.1, 1 wt.-%	600/9.6, 2 wt.-%
			

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As can be observed from Table 3 for pectin particles especially small cylinder ratios resulted in well-shaped particles. Smaller cylinder ratios result in cut cylinders with dimensions which are closer to the lateral dimensions of the targeted spherical droplet form. In this case, only small volumes have to be shaped by surface tension throughout falling instead of large deformation for cylinders with high cylinder ratio. In combination with small nozzle diameter, highest sphericity is obtained (see Table 3: pectin, nozzle diameter 450 µm, cylinder ratio 0.7).

Larger nozzle diameter (1000 µm) results in mainly small, well-shaped particles comparable to those from smaller nozzles but also large, deformed particles. This indicates that breaking of the large primary droplets into smaller secondary droplets occurs during the collection and stirring. The deformation and breaking of large primary particles might be explained by the decreased stability of larger particles. Increasing nozzle diameter results in increased particle volume. Due to the spherical shape of falling droplets, with increasing droplet diameter the volume (and mass) is increased with the diameter to the power of 3, whereas, the cross-sectional area of the particles is increased by diameter to the power of 2. With this, the ratio between volume and cross-sectional area increases with increasing droplet diameter. This change has an impact on the droplet stability during the impact on the surface of the collection bath and during stirring inside the bath. Increasing particle mass results in increasing ratio of particle energy to particle surface. This increased ratio leads to less stability of the droplets. Therefore, the breaking of larger particles is more likely than of smaller particles.

On the other hand, for both systems, with larger nozzle also larger particle diameters and deformed particles are obtained, indicating deformation of unbroken droplets inside the gelation bath before proper gelation occurred. However, smaller nozzle diameter results in nearly no deformed particles and narrower particle size distribution. This difference might be due to the larger impact of a gelled outer layer at small particles. For smaller particles the ratio between the stable outer surface and the volume is smaller than for larger particles, therefore, a stable gelled layer at the outside is more effective for stabilization as for large particles and might help to avoid deformation and destruction of particles during stirring.

High cylinder ratios generally led to deformed and elongated particles. Often tails and flattening of the beads could be observed (compare Table 3: 3 wt.-% pectin, nozzle diameter 500 µm, cylinder ratio of 12.1). This might be explained by too slow transformation of cut cylinders into spherical droplets. Cylinder ratio of 12.1 means cylinders which are 12.1 times higher than their diameter and therefore have quite elongated shape. When the droplets hit the surface of the gelation bath, they might be still elongated. Especially, for alginate particles the combination of large nozzle diameter (500-600 nm) and high cylinder ratios (12.4 and 9.6) results in deformed particles.

It is obvious that nozzle diameter and cylinder ratio have a decisive impact on the particle size and shape. Nevertheless, these two parameters are not sufficient to explain particle shape and size. It is likely that vigorous stirring – as it is needed for particle separation – also causes damage of not yet gelled particles. More uniform flow fields and less turbulence inside the gelation bath could help to improve this situation. Therefore, further studies need to be done to evaluate the impact of these parameters on the particle size and shape.

During collection of pectin particles from calcium chloride solution solid needles could be observed around the particles (Figure 3).

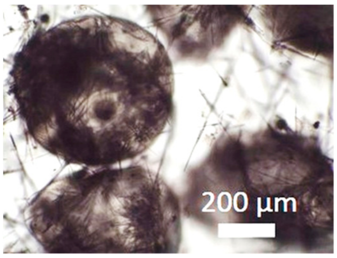

Figure 3: Collected pectin hydrogel particles from diffusion method with solid needles

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These needles were removed during washing, solvent exchange, and drying step. Most likely these needles result from crystallized calcium carbonate. Another observation for both polysaccharides is the formation of bubbles inside many of the particles, especially for spherical ones. The gas was slowly released during the solvent exchange before supercritical drying, nevertheless, included bubbles resulted in particle inhomogeneity. One possible explanation for this phenomenon is that air is partly dissolved in the biopolymer solution during preparation, at the moment of extrusion through the nozzle, the pressure drop leads to degassing of the gas from the solution resulting in gas bubbles in the gelling particle. Another explanation might be that during reshaping to spherical droplets from cut cylinders air is included to the droplets. For the deformed particles it is likely that the gas is released during the deformation and breaking. Included gas bubbles lead to inhomogeneous structure of the particles and might influence their flowing and mechanical properties.

3.3 Internal setting method

In case of internal setting method, polymer solutions were mixed with solid $CaCO_3$ particles and gelation was induced during the contact with an acid in the gelation bath. For neutralized pectin solutions (2 and 3 wt.-%, pH 7), aqueous solution of citric acid (pH 3-4) was used as a collection bath, whereas 30 wt.-% acetic acid was used for alginate. The drop of the pH value in the bath induced the dissolution of $CaCO_3$ and ionotropic gelation of pectin and alginate took place. In this case, the particle size of the dispersed solid $CaCO_3$ is limiting for the processing with the JetCutter. The particles have to be small enough to pass the nozzle and therefore limit the size of the nozzle, which can be used. In our case, $CaCO_3$ had the average size of ca. 1 µm. To avoid blocking inside the nozzle due to agglomerates of $CaCO_3$, appropriate homogenization of the dispersions with e.g. a rotor stator machine is suggested.

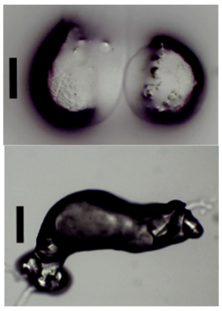
Significant differences between pectin and alginate were observed at low polymer concentration (1 wt.-%). Pectin beads re-dissolved during the washing step due to incomplete gelation and weak particles. Further, after the collection in filter paper and supercritical drying particles with low pectin concentration (1 wt.-%) were agglomerated. Pectin hydrogel particles from 2 and 3 wt.-% solutions and alginate particles (from all used concentrations) were stable and overcame the washing step and solvent exchange without a visible damage.

Gel particles obtained at different combinations of nozzle diameter and cylinder ratio for internal setting method are shown in Table 4.

Table 4: Used nozzle diameter and cylinder ratio and obtained gel particles via internal setting method

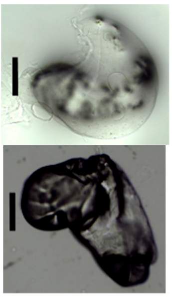
Gel particles obtained from 2 wt.-% amidated pectin solution by internal setting method (nozzle diameter/cylinder ratio, black bar corresponds to 200 µm)

450/1.2



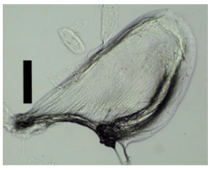
450/1.6

450/1.9

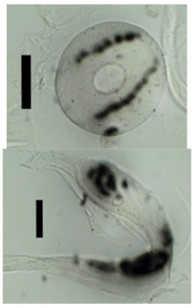


450/3.4

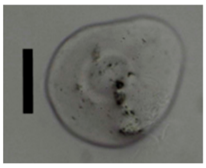
450/3.8



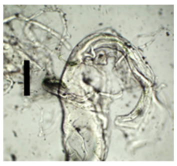
450/8.0



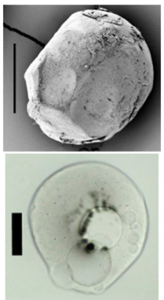
450/11.5



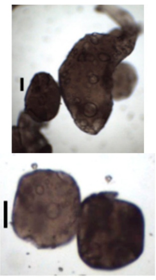
450/11.6



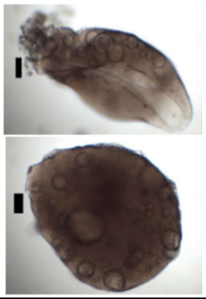
500/0.9



500/4.7

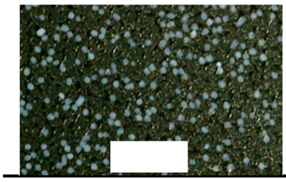


500/9.6

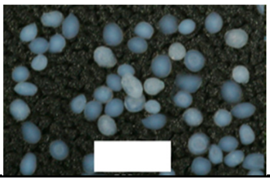


Gel particles obtained from 3 wt.-% sodium alginate solution by internal setting method (nozzle diameter/cylinder ratio, alginate concentration, white bar corresponds to 5 mm)

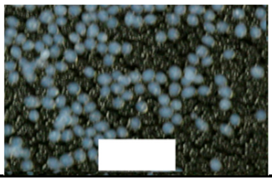
300/8.7



500/6.0



500/9.4



As can be seen from Table 4 for the internal setting method the impact of the cylinder ratio is less pronounced than for the diffusion method. In case of pectin solutions very small cylinder ratio (0.9) results in spherical particles, however, for only slightly higher cylinder ratios (1-2) mainly badly shaped particles were obtained. For the larger nozzle diameter (500 µm) again spherical particles could be produced also for even larger cylinder ratios (4.7, 9.6). Altogether, in nearly every gelation bath, spherical particles could be found. This indicates that the deformation of the particles might occur inside the gelation bath and not during the droplet formation during falling. Especially for alginate solution it was observed that high cylinder ratios (6.0 – 9.4) results in spherical particles for different nozzle diameters.

Generally, the internal setting gelation of pectin seemed to be slower compared to the diffusion method, what resulted in weaker gel particles after the same gelation time. During internal setting

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method, contact with the gelation bath caused the drop of the pH value inside the droplets and subsequent dissolution of distributed $CaCO_3$ particles. Calcium ions are released and induce gelation of pectin molecules in the whole droplet. Due to the required dissolution of $CaCO_3$ particles the gelation process seems to be slower but lead to more homogeneous droplets compared to diffusion method. Nevertheless, it seemed that slower gelation favored deformation of droplets inside the gelation bath. Sheer forces due to stirring of the bath might cause the deformation of the droplets, whereas gelled particles might withstand these forces.

In conclusion, both, diffusion and internal setting method are feasible to be combined with the jet cutting method to produce spherical shaped aerogel particles from pectin and alginate solutions. However, the diffusion method is simpler in preparation and handling of stock solutions in comparison to the internal setting method, where due to the higher viscosities of the solutions and blocking of the nozzle with calcium carbonate, particle production is challenging. Further, especially for pectin, diffusion method seemed to be more favorable in terms of particle deformation and breaking during the process. Thereby, a clear dependency of particle shape and size on the cylinder ratio and nozzle diameter could be observed. In case of alginate solution internal setting method seems to be more independent of the nozzle diameter regarding the particle shape. Nevertheless, spherical alginate particles could be produced also with the diffusion method. Taking into account this fact and also regarding the handling of the process, generally, diffusion method seems to be easier to produce spherical hydrogel particles.

3.4 Aerogel properties

After solvent exchange and supercritical drying aerogel particles were obtained. The specific surface areas of the obtained aerogel particles are shown in Table 5. Obtained specific surface areas are in the range of those of aerogel monoliths (1 wt.-% pectin internal setting method with citric acid: 541 ± 99 m^2/g and 2 wt.-% pectin internal setting method with carbon dioxide: 690 ± 54 and 1 wt.-% alginate internal setting method with carbon dioxide: 592 ± 27 m^2/g) produced in pre-studies. Aerogel particles presented produced via emulsion gelation combined with diffusion and internal setting method in literature show for alginate specific surface areas around 394 m^2/g by diffusion method and 469 – 590 m^2/g by internal setting method [2], [11] and 470 – 593 m^2/g for pectin by diffusion method [16]. Obtained specific surface areas aerogel particles produced by jet cutting method are the same range as for monoliths and particles produced earlier. Further, the high specific surface area is in agreement with the SEM pictures (Figure 4-6) showing highly porous microstructure of obtained aerogels by jet cutting method. Therefore, we conclude that the jet cutting method is feasible to produce spherical aerogel particles from pectin and alginate solutions.

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Table 5: Average specific surface area of produced aerogel particles

Sample preparation	**Specific surface area [m²/g]**	**Standard deviation (*n* ≥ 3) [m²/g]**
3% Pectin in $CaCl_2$ solution	528	58
2% pectin in $CaCl_2$ solution	595	11
2% Pectin in citric acid	558	81
Alginate in $CaCl_2$	537	2 (error of measurement apparatus)
Alginate in acetic acid	593	10

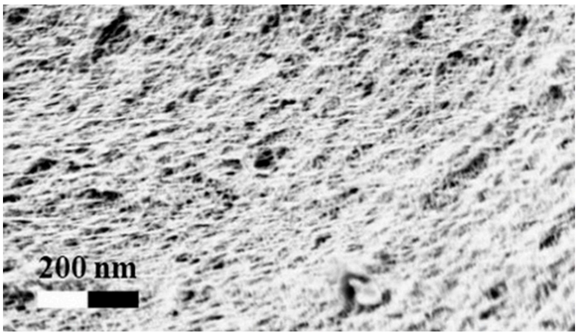

Figure 4: Inner structure of pure pectin aerogel produced via diffusion method

Figure 5: Inner structure of pure amidated pectin aerogel produced via internal setting method

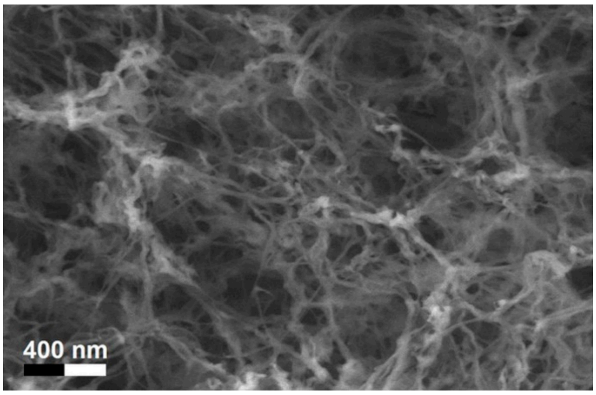

Figure 6: Inner structure of pure alginate aerogel produced via diffusion method

Similar specific aerogel surface areas were obtained with both internal setting and diffusion method.

3.5 Application of aerogels as humidity absorber in drying units of dishwashers

Due to promising results for amidated pectin and alginate during the particle production with the jet cutting system and understanding of the parameters, chitosan aerogel particles were produced to demonstrate the high potential for the application in dishwashers (nozzle diameter 300-700 µm, cylinder ratio 5.3). Produced chitosan aerogel particles are shown in Figure 8. Synthesized chitosan aerogel particles were evaluated as humidity absorbers for the drying step in dishwashers. For this purpose, dishwasher prototypes were prepared. A schematic of a dishwasher designed for the prototype test of aerogel particles is shown in Figure 7. In the dishwasher prototype, which is developed in this study, the humid air is taken from the washing container to the absorption material chamber (with aerogel particles) by a fan. Aerogels inside the absorbent material chamber absorb the water and dried air is transported to the washing container. Before the next washing cycle, regeneration of the aerogel particles will take place inside the absorbent material chamber. The temperature of humid air from the washing container is 45°C and gradually decreases down to room temperature until the end of the cycle. Relative humidity at the beginning of the drying step is 100% and decreases to around 70% within five minutes and further down to 40% until the end of the cycle. A heating unit is attached to the absorbent material chamber for the regeneration of aerogel particles.

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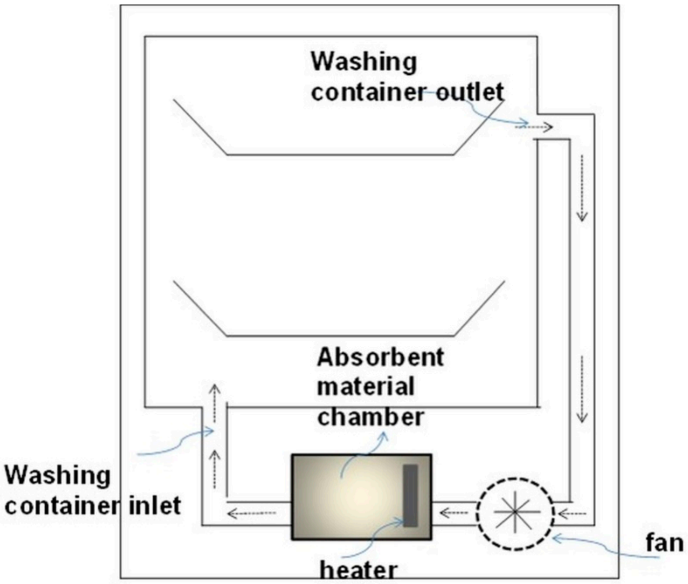

Figure 7: Schematic of a designed dishwasher for the prototype testing of aerogel particles

In order to select the best absorbent aerogel and before incorporating them into the dishwasher, absorption/desorption capacities of the chitosan aerogel particles were characterized in laboratory conditions. Five different chitosan aerogel samples were tested. The aerogel samples were kept in the humidity chamber at 27°C and 80% relative humidity, which is simulating the lowest temperature and relative humidity conditions in a dishwasher during the drying step. The absorption/desorption cycles of the chitosan aerogel sample with the highest absorption capacity are shown in Table 6 (3 wt.-% chitosan, nozzle diameter 700 µm, cylinder ratio 5.3). The average absorption capacity was found to be approximately 19 wt.-%.

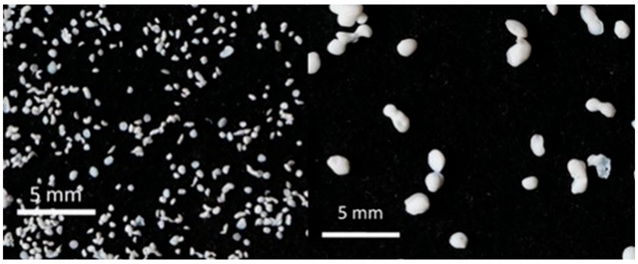

Figure 8: Chitosan aerogel particles (3 wt.-%) via jet cutting method: left: cylinder ratio 5.3, nozzle diameter 300 µm; right: cylinder ratio 5.3, nozzle diameter 700 µm

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Table 6: Absorption and desorption behavior of 3 wt.-% chitosan aerogel particles

Sample	Cycle Number	Absorption [wt.-%]	Desorption [wt.%]
3 wt.-% chitosan aerogel particles	1	21.1	20.1
	2	19.3	17.9
	3	20.1	18.7
	4	19.8	18.1
	5	20.2	17.2
	6	19.3	17.1
	7	19.5	16.9
	8	18.9	17.1
	9	19.1	16.8
	10	19.6	16.1
	11	18.5	16.9
	12	18.9	16.8
	13	19.8	17.5
	14	20.1	17.8
	15	19.4	17.1

It can be observed that absorption and desorption capacity is nearly constant over several cycles of absorption and desorption. First prototype tests resulted in consistent absorption capacities as those in laboratory scale.

This result is promising for the application of aerogel particles in dishwashers for the reduction of total energy consumption. Throughout the whole washing cycle in a conventional dishwasher, the drying step itself consumes a considerable amount of energy (45% of the overall energy consumption in a washing cycle) by heating up the water temperature to approximately 65°C. This energy consumption can be reduced by lowering the heating temperature or even eliminating the heat step completely from the drying step by using water vapour absorbers instead. Tested chitosan aerogels show the potential for the use as water vapour absorbers and therefore, for the reduction of energy consumption.

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4. Conclusions

Spherical aerogel particles from amidated pectin, sodium alginate, and chitosan solutions were successfully produced via jet cutting method and subsequent supercritical drying with CO_2. Aerogels in form of particles with high specific surface areas could be obtained. Both, diffusion and internal setting method of gelation were found to be feasible in combination with the jet cutting technique. A clear dependency of particle shape and size on the jet cutting parameters cylinder ratio and nozzle diameter could be shown. Especially for the diffusion method, low cylinder ratios result in spherical particles. A large nozzle diameter led mainly to an increase of the particle size, but also favored the breaking and deformation due to unstable droplets. Also the internal setting method showed strong dependency on the nozzle diameter regarding particle size, whereas, for the pectin solution even a stronger deformation compared to the diffusion method was observed. Also other parameters like bath stirring velocity and distance between cutting tool and collection bath might have a large impact on the particle shape and destruction. Therefore, further investigations on additional parameters of the jet cutting process and the particle gelation and collection will be done to find the optimal parameters for production of spherical particles of defined particle size with narrow particle size distribution. Nevertheless, it could be shown that the jet cutting method is a promising process to produce large amounts of spherical biopolymer-based aerogel particles. Furthermore, the chitosan aerogel samples synthesized in this study were tested as humidity absorbers in drying units of home appliances, particularly for dishwashers. The average absorption capacity was found to be around 20 wt.-% and nearly stable absorption and desorption capacities were observed over several cycles of absorption and desorption of humid air. Therefore, obtained aerogel particles show great potential for the application in home appliances like dishwashers for the reduction of the energy consumption. Use of water vapour absorbers can help to lower the heating temperature or even eliminate the heating step throughout the drying step in conventional dishwashers and therefore help to reduce the energy consumption.

Author Contributions: "Conceptualization, I.P., P.N., Y.Y., P.G., B.M., I.S.; Investigation, I.P., P.N., Y.Y.; Methodology – particle production, I.P. and P.N.; Methodology – application, Y.Y.; Writing-Original Draft Preparation, I.P., P.N. and Y.Y.; Writing-Review & Editing, P.G., B.M., I.S.; Supervision, P.G., B.M., I.S."

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