Journal of Colloid and Interface Science 568 (2020) 46–53

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

Monodisperse liquid foams via membrane foaming

Laura Carballido, Miriam Lucia Dabrowski, Friederike Dehli, Lukas Koch, Cosima Stubenrauch *

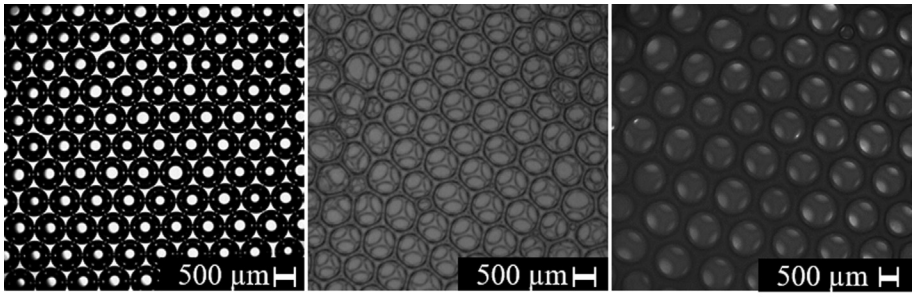
Institute of Physical Chemistry, Pfaffenwaldring 55, 70569 Stuttgart, Germany

HIGHLIGHTS

- First generation of truly monodisperse liquid foams via membrane foaming.
- Membrane pore diameter sets bubble size, while injection rate determines generation rate.
- Output is up to two orders of magnitude larger compared to microfluidics.
- Monodisperse liquid foams can be used for the production of monodisperse solid foams.

GRAPHICAL ABSTRACT

The dispersion cell *LDC-1* by *Micropore Technologies Ltd.* is typically used to produce emulsions via membrane emulsification where the polydispersity index *PDI* can be as low as 10%. Taking a simple surfactant solution and air, the same device was used to synthesize liquid foams by membrane foaming for the first time. We found that the *PDI* is in the monodisperse range (*PDI* < 5%) with three different membrane pore sizes and at moderate air injection rates if no stirrer is employed. Two more continuous phases that possess the potential to be solidified in future work were also tested and resulted in monodisperse liquid foams as well. The investigated method is therefore an improvement to microfluidics which is conventionally utilized to produce monodisperse liquid foams since the output rate of membrane foaming is at least 50–100 times higher.



Monodisperse liquid foams produced via the dispersion cell

ARTICLE INFO

Article history:
Received 8 January 2020
Revised 10 February 2020
Accepted 11 February 2020
Available online 12 February 2020

Keywords:
Membrane foaming
Dispersion cell
Monodisperse liquid foam
High output

ABSTRACT

Hypothesis: It is possible to generate fairly monodisperse liquid foams by a dispersion cell, which was originally designed for the generation of fairly monodisperse emulsions. If this is the case, scaling-up the production of monodisperse liquid and solid foams will be no longer a problem.
Experiments: We used the dispersion cell - a batch process - and examined the influence of stirrer speed, membrane pore diameter and injection rate on the structure of the resulting liquid foams. We used an aqueous surfactant solution as scouting system. Once the experimental conditions were known we generated gelatin-based liquid foams and methacrylate-based foamed emulsions.
Findings: We found that (a) the bubble size of the generated liquid foams can be adjusted by varying the membrane pore diameter, (b) no stirrer should be used to obtain monodisperse foams, and (c) the bubble size is not influenced by the air injection rate. Since (i) the output for all investigated systems is up to two orders of magnitude larger compared to microfluidics and (ii) the membrane technology can very easily be scaled-up if run in a continuous process, the use of membrane foaming is expected to be heavily used for the generation of monodisperse liquid and solid foams, respectively.

* Corresponding author.
E-mail address: cosima.stubenrauch@ipc.uni-stuttgart.de (C. Stubenrauch).

https://doi.org/10.1016/j.jcis.2020.02.036
0021-9797/

1. Introduction

Liquid foams and emulsions are used in numerous applications in our daily life e.g. in pharmaceuticals [1], cosmetics [2] or in the food industry [3]. Their properties such as tactility or stability often depend on the bubble or droplet size as well as on the bubble or droplet size distribution. Usually, foams or emulsions are produced using energy intensive rotor-stator systems, high speed stirrers or static mixers [4–6]. While being easy to set up and having a high material output, these devices produce large shear forces and are thus not suitable for sensitive compounds such as proteins [7]. Furthermore, broad bubble size distributions are generated [5]. On the lab scale, these issues are addressed by using microfluidics, with which foams or emulsions are generated by pushing a gas or a liquid phase through a microfluidic chip. Due to the constraint induced by the micrometric dimensions, bubbles or droplets are pinched-off. Due to the periodic nature of the pinch-off, uniform foams and emulsions with extremely narrow bubble and droplet size distributions can be generated [8–11] . Even though the parallelisation of microfluidics can lead to a higher production rate, the scale-up of this technique still remains a challenge. Especially the generation of uniform liquid foams based on polymerizable compounds is very interesting if the structure of the liquid foam is preserved during polymerization [11,12]. The resulting materials can potentially be applied in e.g. tissue engineering or for thermal and acoustic insulation purposes as monodisperse foams are hypothesized to have unique properties [8,13]. However, superior material properties can only be examined if large samples can be produced in a reasonable amount of time. Thus, scaling-up the production of monodisperse foams is of particular interest.

For emulsions, this scale-up challenge, i.e. the generation of a higher amount of emulsion while maintaining a narrow droplet size distribution, has been addressed by developing a stirred cell membrane emulsification device. In this technique, the dispersed phase is pushed through the pores of a flat disc membrane while a paddle stirrer positioned above the membrane induces a shear force which results in droplet detachment. Fig. 1 shows a schematic drawing of the dispersion cell.

The generation of both oil-in-water (o/w) and water-in-oil (w/o) emulsions using this setup has been examined thoroughly [14–20]. Compared to conventional emulsion production (*PDI* of 120%) the droplet size distributions of emulsions produced with this setup are significantly narrower (*PDI*s of 10–26%) [14,15,18,19]. In contrast to that, microfluidics enables the generation of emulsions with *PDI*s < 5% [8,10]. As mentioned before, the extremely low monodispersity is reached at the expense of the production rate which is in the range of microliters per minute [21]. For membrane emulsification, the production rate is in the range of tens of millilitres per minute [21].

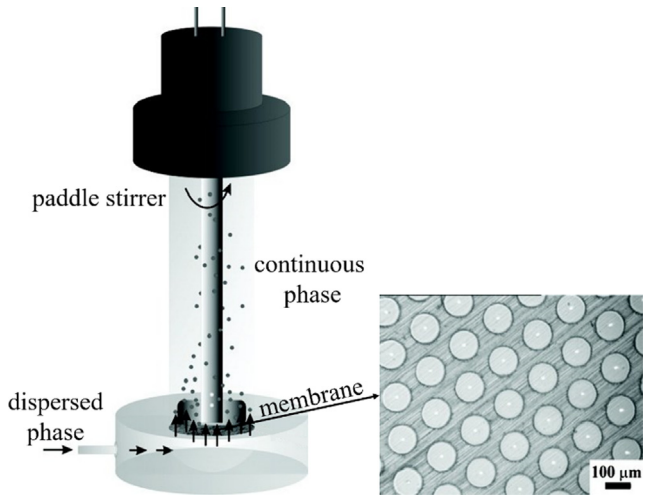


Fig. 1. Schematic drawing of the dispersion cell (Adapted with permission from [14] R.G. Holdich, M.M. Dragosavac, G.T. Vladisavljević, S.R. Kosvintsev, Membrane Emulsification with Oscillating and Stationary Membranes, Ind. Eng. Chem. Res. 49 (2010) 3810–3817.). Copyright (2010) American Chemical Society.

To the best of our knowledge, the generation of foams with a stirred cell membrane device has not been examined yet. In contrast to that, the concept of membrane foaming itself has been investigated in several studies using a tubular or a rotating membrane [7,22,23]. However, only moderately narrow bubble size distributions can be generated and the experimental parameters cannot be varied as conveniently as with the stirred cell membrane device. Furthermore, the experimental setup is quite large and cumbersome. Thus, the objective of this study was to examine the generation of liquid foams using membrane foaming with the stirred cell. To this end, different experimental parameters, namely the stirrer speed, the membrane pore diameter and the injection rate of the gas phase, were examined. An aqueous solution containing 5 wt% of the surfactant Plantacare 2000 UP was used as a scouting system. Furthermore, the generation of liquid foams with a polymerizable continuous phase was investigated. In the first case, the continuous phase was an aqueous solution of 5 wt% methacryloylated gelatin (GM). In the second case, the continuous phase was an emulsion where the dispersed phase of the emulsion was 1,4-butandiol dimethacrylate (1,4-BDDMA) and the continuous phase of the emulsion was water. In previous studies, foams based on these systems were produced via microfluidics and subsequently polymerized via UV-initiated radical polymerization [11,12]. Being able to produce similarly monodisperse liquid foams via membrane foaming, one can easily – as already mentioned – scale-up the production of very promising macroporous materials.

2. Experimental part

2.1. Materials

Plantacare 2000 UP was donated by *Cognis* (now BASF). Gelatin (type B, 232 bloom) was purchased from Gelita. Methacryloylated gelatin (GM10) with a degree of methacrylation of 1.08 mmol g^{-1} was synthesized according to Claasen et al. [24]. 1,4-Butanediol dimethacrylate (1,4-BDDMA, 95%), glycerol (≥99%), and sodium dodecylsulfate (SDS, ≥99%) were purchased from *Sigma Aldrich*. Bi-distilled water was used for all experiments and is further named water. All chemicals were used as received without purification.

2.2. Generation of liquid foams and foamed emulsions

Liquid Foams. For the generation of liquid foams, we prepared 20 mL of two solutions. (1) An aqueous solution containing 5 wt% Plantacare 2000 UP and (2) an aqueous solution containing 5 wt% methacryloylated gelatin (with respect to the mass of water) and 0.1 wt% Plantacare 2000 UP (with respect to the mass of water) were prepared. The aqueous solutions were foamed with air via membrane foaming (see Section 2.3).

Foamed Emulsions. For the generation of foamed emulsions, 20 mL of a 1,4-BDDMA-in-water emulsion was formulated by mixing 65 vol% 1,4-BDDMA, 30 vol% water and 5 vol% glycerol with 5 wt% SDS (with respect to the total mass of the emulsion) for 30 min. The emulsion was homogenized once by using a *Bandelin Sonoplus HD-2200* for 40 s at a power of about 30%. The emulsion was cooled with an ice-bath during homogenization. The

1,4-BDDMA-in-water emulsion was then foamed with air via membrane foaming (see Section 2.3).

2.3. Membrane foaming with the dispersion cell

Foaming was performed with a *LDC-1* dispersion cell purchased from *Micropore Technologies Ltd*. The device consists of an injection chamber where the membrane is placed, a glass cylinder which serves as sampling chamber, and a stainless steel stirrer (see Fig. 1). The membrane has to be immersed in the continuous phase of the foam and had to be ultrasonicated prior to use to wet the membrane with the continuous phase and to remove residual gas bubbles in the membrane pores. The continuous phase was transferred into the sampling chamber of the device and a syringe pump (*Pump 11 Elite* from *Harvard Apparatus*) equipped with a 20 mL syringe (from *Braun*) was used to press air (dispersed phase) through the membrane into the continuous phase. For the aqueous surfactant solution, flow rates between 5 mL min^{-1} and 85 mL min^{-1} were tested with three hydrophilic stainless steel membranes with pore diameters of 10 μm, 20 μm, and 100 μm. Stirrer speeds were set from 0 V to 12 V. Gelatin-based liquid foams and methacrylate-based foamed emulsions, on the other hand, were generated by adjusting the flow rate of the dispersed phase to 5 mL min^{-1} and by using only the membrane with a pore size of 20 μm.

2.4. Optical microscopy

After foaming, micrographs of a small amount of foam were taken with a *Nikon SMZ 745T* Microscope equipped with a *Microton EoSens CL MC1362* high-speed camera and a light source from *Schott* (*KL 1500 compact*) combined with a *mitos microsope stage* from *Dolomite*. The software of the high-speed camera *Mikroton MBDirector2 KIT* was provided by Mikroton.

2.5. Determination of bubble diameters

The mean bubble diameter was determined by measuring the areas of the bubbles A_{bubble} with the software *ImageJ* (automatically or manually) and calculating the diameter of each bubble d_{bubble} by using the equation of a circle

$$d_{bubble} = 2 \times \sqrt{\frac{A_{bubble}}{\pi}}. \quad (1)$$

Then, the arithmetic mean $\bar{d}_{bubble}$ and its standard deviation σ_{bubble} were calculated for at least 40 bubbles. The polydispersity of the liquid foams and foamed emulsions was determined by calculating the polydispersity index (*PDI*) according to [25,26] with

$$PDI = \frac{\sigma_{bubble}}{\bar{d}_{bubble}} \times 100. \quad (2)$$

The bubbles are presumed to be monodisperse if the *PDI* is lower than 5% [25].

3. Results and discussion

The dispersion cell *LDC-1* from *Micropore Technologies Ltd.* was used to generate monodisperse foams with three different systems. These were (1) an aqueous solution containing 5 wt% Plantacare 2000 UP, (2) an aqeuous solution containing 5 wt% methacryloylated (GM10) gelatin and 0.1 wt% Plantacare 2000 UP, and (3) a 1,4-BDDMA-in-water emulsion. Each of the three systems acts as the continuous phase of the foam, while the dispersed phase was air in all cases. The first system, air dispersed in an aqueous solution of 5 wt% Plantacare 2000 UP (1), helped us to become acquainted with the dispersion cell *LDC-1* and acted as a scouting system for more complex continuous phases. Here, we investigated the influence of the stirrer speed (3.1.1), the membrane pore diameter (3.1.2), and the air injection rate (3.1.3) on the bubble size and bubble size distribution. Our goal was to find a set of parameters with which a polydispersity as low as possible and an output rate as large as possible could be obtained. The other two continuous phases, an aqueous solution containing 5 wt% methacryloylated (GM10) gelatin and 0.1 wt% Plantacare 2000 UP ((2), Section 3.2.1) and a 1,4-BDDMA-in-water emulsion ((3), Section 3.2.2), were chosen because they were already used in our group for the synthesis of monodisperse liquid foams via microfluidics.

3.1. Scouting system

3.1.1. Stirrer speed

One parameter influencing the bubble size and bubble size distribution is the stirrer speed which is controlled by the voltage applied onto the stirrer. Thus, we will use the term "stirrer voltage" from now on. In the case of membrane emulsification, the stirrer is required to create a shear stress at the membrane surface which detaches the droplets from the membrane. Table 1 shows the correlation between the stirrer voltages (in volt V) displayed in this paper and the corresponding stirrer speeds (in rounds-*per*-minute rpm) and shear stresses (in Pascal Pa) occuring at the membrane surface. The data in Table 1 was taken from the manual of the dispersion cell *LDC-1* which was provided by *Micropore Technologies Ltd.* [27].

Fig. 2 (left) shows monolayers of bubbles that were obtained when the stirrer speed was varied between 0 V and 12 V for a membrane pore diameter of 20 μm and a constant air injection rate of 5 mL min^{-1}. Fig. 2 (right) shows the corresponding bubble size distributions.

The micrograph in the top left in Fig. 2 shows that when no stirrer is used (stirrer voltage is 0 V), the foam is monodisperse. When the stirrer voltage is systematically increased to 4 V, 8 V, and 12 V, the bubbles become increasingly smaller and more polydisperse. The changes of the bubble size distribution and of the *PDI* are shown in Fig. 2 (right). Using no stirrer, one obtains bubble diameters which are about 33–40 times larger than the membrane pore diameter and a narrow bubble size distribution. If, on the other hand, the stirrer voltage is increased to 12 V, the bubble diameters are 5–30 times larger than the membrane pore diameter and have a broad bubble size distribution. We argue that higher stirrer voltages result in the mean bubble diameter becoming smaller because the rotor "cuts" the air stream traversing the membrane more often, resulting in smaller parcels. The same behavior can be observed in membrane emulsification with the dispersion cell *LDC-1* from *Micropore Technologies Ltd.* as well as other devices [14–20,28–32].

However, the development of the bubble size distribution is in contrast to what has been observed for the droplet size distribution in membrane emulsification. In the latter case, the droplets become less polydisperse [15], traverse a minimum polydispersity [28,29], or remain at a constant level of monodispersity [16,19]

Table 1
Correlation between the stirrer voltage, the stirrer speed and the shear stress occuring at the membrane surface for an aqueous surfactant solution as continuous phase [27].

Stirrer voltage/V	Stirrer speed/rpm	Shear stress/Pa
4	329	1.8
6	552	4.1
8	784	7.1
10	1015	10.6
12	1241	14.4
14	1470	18.7

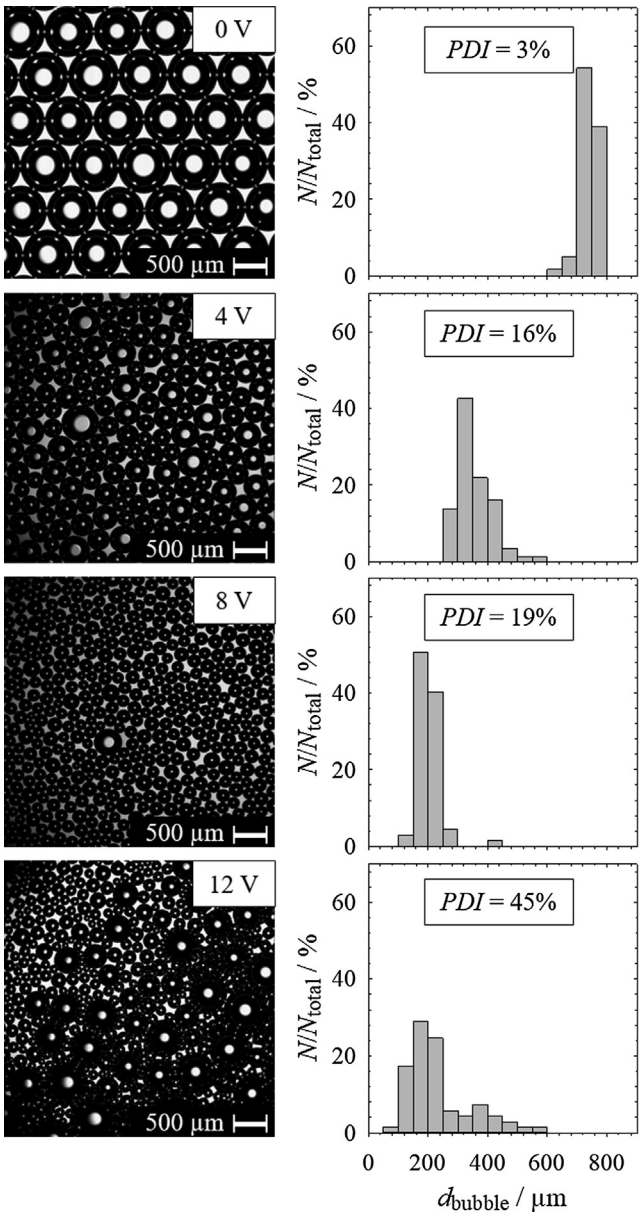


Fig. 2. (left) Micrographs of bubble monolayers obtained by foaming an aqueous solution containing 5 wt% Plantacare 2000 UP via the dispersion cell *LDC-1* with a membrane pore diameter of 20 µm, an injection rate of 5 mL min^{-1}, and different stirrer voltages. (right) The corresponding bubble size distributions (given are the bubble diameters d_{bubble}).

when the stirrer speed is increased. Additionally, when no stirrer voltage is applied, no droplets can be produced at all and two separate phases emerge. In membrane foaming, on the other hand, the highest monodispersity is obtained when no stirrer is used, while using a stirrer and increasing its voltage leads to bubbles becoming increasingly polydisperse. Obviously, the shear stress caused by the stirrer destroys the bubbles. We attribute this behavior to "overwhipping" which is a well-known phenomenon in biological foams [33–36]. In a nutshell, the shear stress is too high and already destroys a portion of the bubbles in the moment they are formed.

3.1.2. Membrane pore diameter

Another parameter influencing the bubble size and the bubble size distribution is the membrane pore diameter. We took two more membranes with membrane pore diameters of 10 µm and 100 µm and carried out the same experiments as described in Section 3.1.1. As a reminder, the membrane pore diameter in Section 3.1.1 was 20 µm. The development of the mean bubble diameter and its *PDI* as function of the stirrer voltage is depicted in Fig. 3 for all three membrane pore diameters.

Fig. 3 shows that the development of the mean bubble diameter as function of the stirrer voltage is the same for all three membranes. In all cases, the mean bubble diameter decreases when the stirrer voltage is increased, while at the same time the *PDI* increases, i.e. the foam becomes more polydisperse. Thus, if one wants to produce monodisperse foams with the dispersion cell *LDC-1*, no stirrer should be used. In other words, if one wants to change the mean bubble diameter, this should not be done by varying the stirrer speed but by other means as discussed in the following. Looking at Figs. 3 and 4, one sees that the *PDI* is ~5% for all three membrane pore diameters when no stirrer was used, i.e. that the bubbles in these samples are monodisperse. The micrographs of bubble monolayers of these samples and the corresponding bubble size distributions are depicted in Fig. 4.

The obtained values of the *PDI* are surprising if one compares membrane foaming and membrane emulsification. In the latter

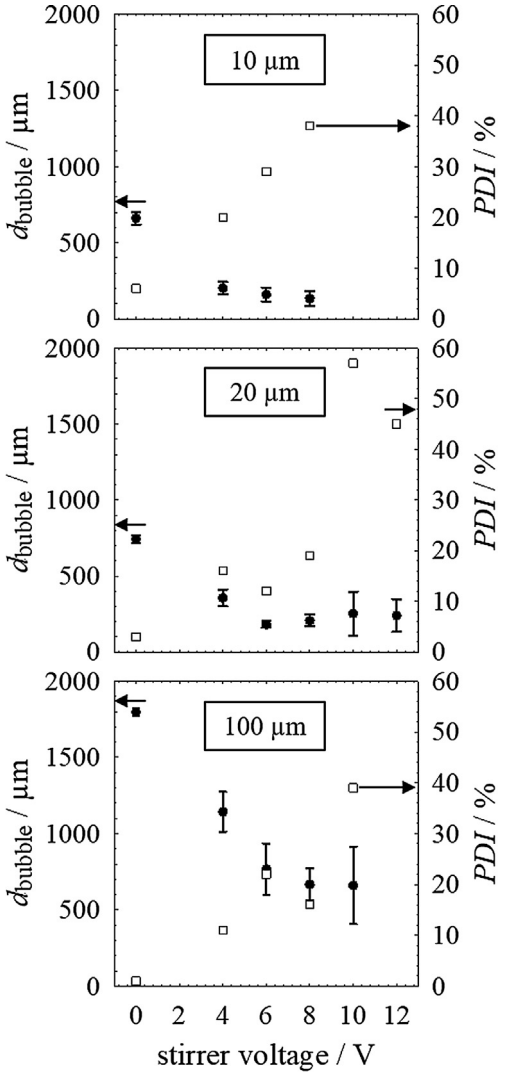


Fig. 3. Mean bubble diameters d_{bubble} and their standard deviation (circles, black) and *PDI* (squares, white) as function of the stirrer voltage for membrane pore diameters of 10 µm (top), 20 µm (middle), and 100 µm (bottom).

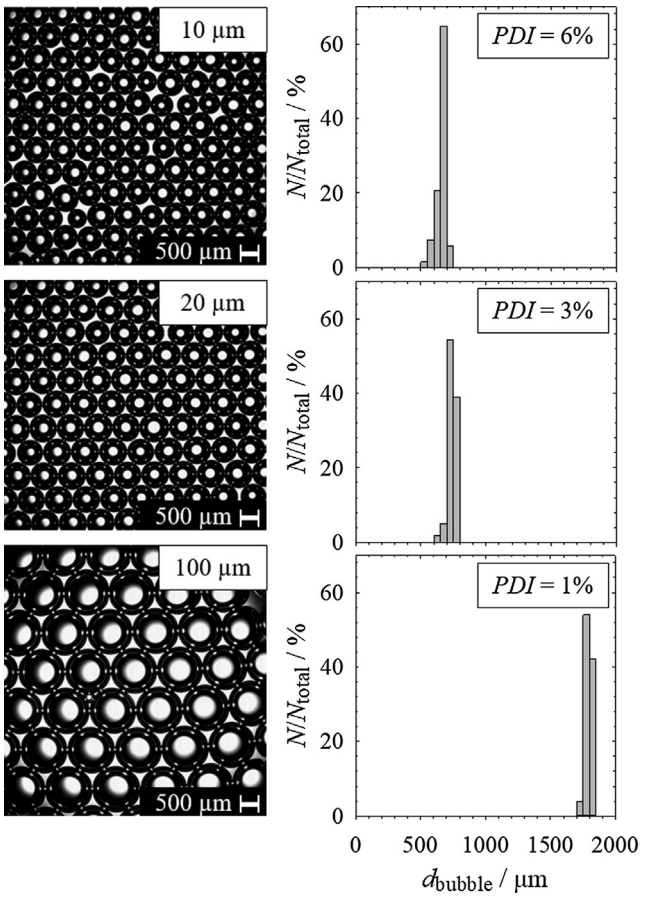


Fig. 4. (left) Micrographs of bubble monolayers obtained by foaming an aqueous solution containing 5 wt% Plantacare 2000 UP via the dispersion cell *LDC-1* with an injection rate of 5 mL min^{-1}, no stirrer, and a membrane pore diameter of 10 µm (top), 20 µm (middle), and 100 µm (bottom). (right) The corresponding bubble size distributions (given are the bubble diameters d_{bubble}).

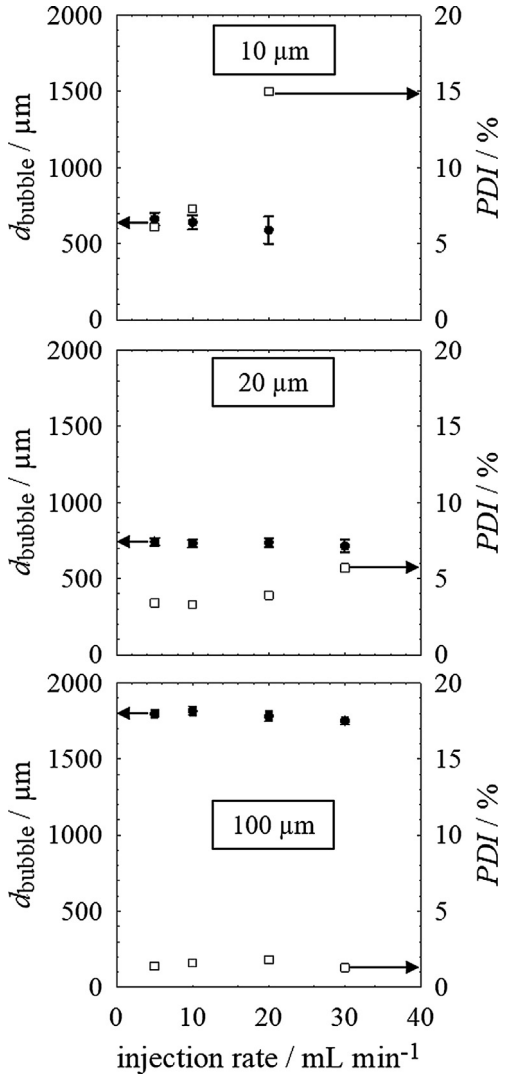


Fig. 5. Mean bubble diameters d_{bubble} and their standard deviation (circles, black) and *PDI* (squares, white) as function of the air injection rate for membrane pore diameters of 10 µm (top), 20 µm (middle), and 100 µm (bottom).

case, the *PDI* cannot be decreased further than ~10% with a dispersion cell [16,19]. In contrast, the *PDI* can be as low as 1% with membrane foaming. As expected, an increase of the membrane pore diameter leads to likewise increased bubble diameters. When the air injection rate is set to 5 mL min^{-1}, the ratio between the mean bubble diameter and the membrane pore diameter is ~70 for a membrane pore diameter of 10 µm, ~40 for a membrane pore diameter of 20 µm, and ~18 for a membrane pore diameter of 100 µm. Thus, this ratio decreases when the membrane pore diameter is increased.

3.1.3. Air injection rate

From membrane emulsification, it is known that the injection rate of the dispersed phase can also change the mean droplet diameter. Thus, we investigated the influence of the air injection rate on the mean bubble diameter. Fig. 5 shows the development of the mean bubble diameter and the corresponding *PDI* as function of the air injection rate for membrane pore diameters of 10 µm (top), 20 µm (middle), and 100 µm (bottom). As already mentioned before, no stirrer was used for the generation of these samples.

Fig. 5 shows that increasing the air injection rate does not substantially change the average bubble diameter for all membranes, while it increases the *PDI* of the bubbles for the two membranes with smaller pores. With the membrane with the largest pores, the *PDI* remains at a low value even when the air injection rate is increased. Note that in publications about membrane emulsification, an increased injection rate leads to larger droplets [16–19,28,30,32]. The reason is the fact that more liquid per time is pumped through the membrane. In our case, we explain the constant mean bubble diameter with a quasi-static regime. In Drenckhan et al., the quasi-static regime is described as a regime where " [...] the flow velocities are sufficiently small so that the system can be assumed to progress via a sequence of static states. Such processes are therefore independent of the flow velocities" [37]. Thus, our tested air injection rates must be small enough for the bubbles to be generated in the quasi-static regime. Although the air injection rates tested by us do not change the bubble size, they can be used to increase the production rate. With the two smaller membrane pore diameters, the *PDI* remains in the monodisperse range until a certain threshold above which the *PDI* starts to increase. This threshold appears at an air injection rate of 20 mL min^{-1} for a membrane pore diameter of 10 µm and at 25 mL min^{-1} for a membrane pore diameter of 20 µm. No air injection rates higher than these thresholds were investigated. For a membrane pore diameter of 100 µm, no such threshold is reached even at the highest used air injection rate of 85 mL min^{-1}. Note that for reasons of clarity, the bubble diameter (1624 ± 40 µm) and the *PDI* (2%) at an air injection rate of 85 mL min^{-1} are not shown in Fig. 5. By increasing the membrane pore diameter, the

air injection rate can be increased to higher values without influencing neither the bubble size nor the *PDI*. For the two smaller membrane pore diameters of 10 μm and 20 μm, a compromise between minimized polydispersity and maximized production rate has to be found. However, we want to emphasize that the output at the lowest air injection rate of 5 mL min^{-1} is still roughly 50 to 100 times higher than that of microfluidics which is typically used to produce monodisperse foams. In other words, we are able to produce liquid foams with monodisperse bubbles in the range of hundreds of milliliters per hour and can adjust the bubble size by simply changing the membrane pore diameter! With the highest air injection rate of 85 mL min^{-1}, we can even produce up to seven liters per hour of a foam with mondisperse bubbles with a membrane pore diameter of 100 μm. To our best knowledge, this has not been achieved so far.

To sum up Section 3.1, monodisperse foams can be produced with the dispersion cell *LDC-1* by using no stirrer and applying low air injection rates. The diameter of the bubbles in the foam is nearly exclusively controlled by the membrane pore diameter. We transferred this knowledge onto the production of foams with more complex continuous phases which we will discuss in Section 3.2.

3.2. Liquid foams of more complex systems

We tried to transfer the results from our scouting system to more complex systems whose liquid foams can be solidified. As a reminder, the two chosen continuous phases were (1) an aqueous solution containing 5 wt% methacryloylated (GM10) gelatin and 0.1 wt% Plantacare 2000 UP (Section 3.2.1) and (2) a 1,4-BDDMA-in-water emulsion (Section 3.2.2). Note that the focus of this study was on the generation of monodisperse liquid foam templates at high output rates (hundreds of milliliters per hour) which is why the synthesis of monodisperse solid foams via templates generated with the dispersion cell will be dealt with in future work. Further note that for both systems we used a membrane pore diameter of 20 μm and an air injection rate of 5 mL min^{-1}. We used these parameters since the produced bubble sizes are closer to the ones we already know from microfluidics [11,12] and because the synthesized liquid foams "only" serve as a proof of concept.

3.2.1. Gelatin methacryloyl (GM)-Based liquid foams

Polymer foams made from bio-based polymers are promising materials for biomedical applications. For example, liquid foams based on methacryloylated gelatin are of great interest as the chemical modification of the polymer chains results in a significantly lower gel point of the aqueous solution compared to non-modified gelatin [38]. Thus, low viscous aqueous solutions of the polymer can be generated at room temperature. The chemical modification of the polymer also allows for the cross-linking of the polymer chains by radical polymerization [39]. The resulting materials can potentially be used e.g. as scaffolds for tissue engineering, as filtering materials, as adsorbens, or as lightweight packaging material. The generation of monodisperse hydrogel foams and solid foams via UV initiated radical polymerization of monodisperse liquid foams based on methacryloylated gelatin was reported previously [11]. To increase the efficiency of the template generation for industrial or biomedical applications, i.e. from ~5 mL h^{-1} in [11] up to 400 mL h^{-1} in this paper, we tried to generate a monodisperse liquid GM-based foam via membrane foaming. Fig. 6 shows a monodisperse liquid GM-foam that was generated with an air injection rate of 5 mL min^{-1} and a membrane pore diameter of 20 μm.

The micrograph in Fig. 6 shows a liquid foam containing uniform-sized bubbles with a mean diameter of 830 μm ± 50 μm. The bubbles order in a hexagonal closed-packed structure due to their uniform sizes. The calculated *PDI* of 6% as well as the narrow bubble size distribution mean that the foam is fairly monodisperse. Thus, membrane foaming via the dispersion cell LDC-1 is suitable to generate monodisperse liquid GM-based foams. Please note that compared to microfluidics the LDC-1 is a batch device, which not only facilitates the production process of monodisperse liquid foams but also allows for an easy scale-up production even beyond 400 mL h^{-1}.

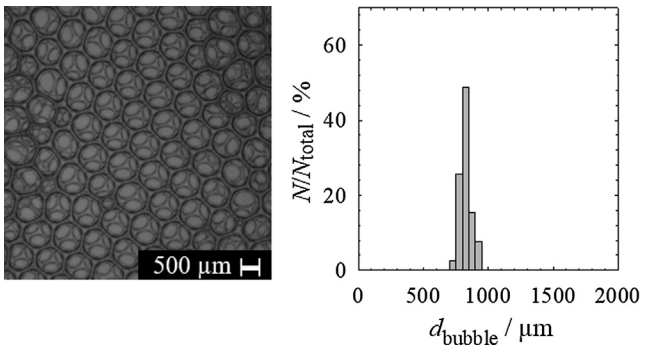


Fig. 6. (left) Micrograph of a GM-based liquid foam whose aqueous phase contains 5 wt% methacryloylated gelatin (with respect to the mass of water) and 0.1 wt% Plantacare 2000 UP (with respect to the mass of water) obtained via membrane foaming without stirrer, an injection rate of 5 mL min^{-1}, and a membrane pore diameter of 20 μm. (right) The corresponding bubble size distribution (given are the bubble diameters d_{bubble}).

3.2.2. Foamed 1,4-BDDMA-in-Water emulsions

Another point worth investigating via the dispersion cell device was the generation of foamed emulsions. So far, polymer foams based on foamed emulsion templates were only synthesized from styrene [10,40–42] and 1,4-butanediol dimethacrylate (1,4-BDDMA) [12]. The templates were generated via mechanical whipping [12,40] or via microfluidics [10,41,42] and subsequently polymerized. The first generation method leads to polydisperse polymer foams [12,40], while the latter one leads to highly monodisperse polymer foams [10,41,42] with controllable pore diameters at the cost of low production rates. To clarify, the generation of monodisperse styrene-based foamed emulsions via microfluidics is limited to 6 mL h^{-1} [42] which compared to the batch device used in the paper at hand is not application-oriented. According to *Micropore Technologies* [43], a total volume of emulsion of roughly 100 mL can be generated at once with the dispersion cell (a batch process), while hundreds or thousands of kilograms of emulsion per hour can be generated by using continuous membrane-based processes. Due to the hazardous properties of styrene, the harmless 1,4-BDDMA was used in this study. First, a 1,4-BDDMA-in-water emulsion was generated as explained in Section 2.2 and foamed via membrane foaming with the dispersion cell *LDC-1* (see Section 2.3) without stirring. The injection rate of the dispersed phase was 5 mL min^{-1} and the bubbles were generated with a membrane pore diameter of 20 μm. Fig. 7 shows the micrograph of the resulting foamed emulsion and its corresponding bubble size distribution.

The micrograph on the left-hand side of Fig. 7 shows an ordered arrangement of uniform bubbles with a large distance between them. The "blurry" background is caused by the layers below. The calculation of the mean bubble diameter and of the *PDI* lead to 1069 μm ± 39 μm and 4% which is indeed quite monodisperse. Comparing the mean bubble diameters obtained with our scouting system, 740 μm ± 25 μm (*PDI* = 3%) in Section 3.1.2, with the gelatin methacryloyl in Section 3.2.1, 830 μm ± 50 μm (*PDI* = 6%), and with the foamed 1,4-BDDMA-in-water emulsion, one sees an increase of the bubble diameter. We have no explanation yet for this

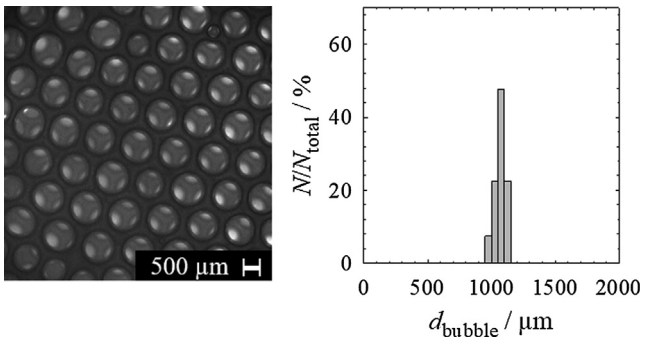


Fig. 7. (left) Micrograph of a foamed emulsion consisting of 65 vol% 1,4-BDDMA, 30 vol% water, 5 vol% glycerol and containing 5 wt% SDS (with respect to the mass of the continuous phase) obtained via membrane foaming without stirrer, at an injection rate of 5 mL min^{-1}, and with a membrane pore diameter of 20 µm (right). The corresponding bubble size distribution (given are the bubble diameters d_{bubble}).

difference. By using the dispersion cell instead of microfluidics, the output of monodisperse foam was increased from ~10 mL h^{-1} to ~400 mL h^{-1}.

To sum up Section 3.2, it was possible to synthesize monodisperse liquid foam templates of both (1) an aqueous solution containing 5 wt% methacryloylated (GM10) gelatin and 0.1 wt% Plantacare 2000 UP and (2) a 1,4-BDDMA-in-water emulsion. Compared to their microfluidic counterparts with a similar monodispersity, the output rates were increased by a factor of (1) 80 and (2) 40, respectively.

4. Conclusion and outlook

In the paper at hand, a purchasable dispersion cell originally designed for membrane emulsification was used to generate monodisperse foams. A monodisperse foam is desirable in applications like tissue engineering where uniform-sized pores enable a homogeneous cell growth and an overall homogeneous scaffold [44]. However, microfluidics, which is the conventional method for producing monodisperse foams, does not exhibit high enough production rates to actually produce monodisperse foams on an industrial scale. Therefore, we investigated a membrane-based technology with which – if run in a continuous process – the production rate of fairly monodisperse foams can be scaled-up. We started with investigating the possibilities and limits of the dispersion cell for generating liquid foams by using an aqueous solution containing Plantacare 2000 UP as our scouting system. The scouting system was foamed with air. The stirring speed, the membrane pore diameter, and the injection rate of the dispersed phase were varied in order to obtain a high output of monodisperse foams. We found that stirring during foaming does more harm than help to create monodisperse bubbles, i.e. the best results were obtained without stirring. Unexpectedly, the injection rate had no impact on the bubble size. Thus, the bubble size is only controllable with the membrane pore diameter, while the injection rate allows to play around with the production rate. Increasing the membrane pore diameter from 10 µm via 20 µm to 100 µm at a constant injection rate of 5 mL min^{-1} led to monodisperse bubbles with increasing diameters from 661 ± 41 µm via 740 µm ± 25 µm up to 1797 µm ± 41 µm.

After having investigated our scouting system, we tried to transfer these results to more complex systems which are suitable for solidification. Thus, we foamed (1) an aqueous solution of 5 wt% gelatin metharyloyl (GM) and 0.1 wt% Plantacare 2000 UP and (2) a 1,4-butanediol dimethacrylate (1,4-BDDMA)-in-water emulsion containing 65 vol% 1,4-BDDMA via membrane foaming with a membrane pore diameter of 20 µm. We obtained GM-based monodisperse liquid foams with a mean bubble diameter of 830 µm ± 50 µm and a *PDI* of 6% and monodisperse 1,4-BDDMA-based foamed emulsions with a mean bubble diameter of 904 µm ± 93 µm and a *PDI* of 10%.

To sum up, membrane foaming is a promising method to generate monodisperse liquid foams and foamed emulsions. Using a membrane-based batch process – as in the study at hand – the output is about hundreds of milliliters per hour which is up to 100 times larger than the output of a microfluidic device [11,42]. Moreover, it is possible to increase the output rate even further to hundreds or thousands of kilograms per hour by using membrane-based continuous processes [43]. Comparing membrane foaming with microfluidics, one sees that the generation of well-defined bubble sizes with membrane foaming is possible only by using membranes with different pore diameters and not by changing the stirrer speed or the air injection rate. In future work, we will synthesize monodisperse polymer foams via liquid foam templates generated with the dispersion cell and subsequently polymerized.

CRediT authorship contribution statement

Laura Carballido: Investigation, Visualization. **Miriam Lucia Dabrowski:** Writing - original draft, Investigation, Visualization. **Friederike Dehli:** Writing - original draft, Investigation, Visualization. **Lukas Koch:** Writing - original draft, Visualization. **Cosima Stubenrauch:** Writing - review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

We are thankful to A. Kerr from *Micropore Technologies* for sharing his experimental know-how as regards the handling of the device.

References

[1] B.A. Khan, N. Akhtar, H.M.S. Khan, K. Waseem, T. Mahmood, A. Rasul, M. Iqbal, K. Haroon, Basics of pharmaceutical emulsions: A review, Afr. J. Pharm. Pharmacol. 5 (25) (2011) 2715–2725.
[2] A. Arzhavitina, H. Steckel, Foams for pharmaceutical and cosmetic application, Int. J. Pharm. 394 (1–2) (2010) 1–17.
[3] E. Dickinson, Food emulsions and foams: stabilization by particles, Curr. Opin. Colloid Interface Sci. 15 (1–2) (2010) 40–49.
[4] W. Hanselmann, E. Windhab, Flow characteristics and modelling of foam generation in a continuous rotor/stator mixer, J. Food Eng. 38 (4) (1998) 393–405.
[5] M. Laporte, D. Valle, C. Loisel, S. Marze, A. Riaublanc, A. Montillet, Food hydrocolloids rheological properties of food foams produced by SMX static mixers, Food Hydrocoll. 43 (2015) 51–57.
[6] H. Karbstein, H. Schubert, developments in the continuous mechanical production of oil-in-water macro-emulsions, Chem. Engineer. Process: Process Intensificat. 34 (3) (1995) 205–211.
[7] A. Bals, U. Kulozik, The influence of the pore size, the foaming temperature and the viscosity of the continuous phase on the properties of foams produced by membrane foaming, J. Membr. Sci. 220 (1–2) (2003) 5–11.
[8] M. Costantini, C. Colosi, J. Guzowski, A. Barbetta, J. Jaroszewicz, M. Dentini, P. Garstecki, Highly ordered and tunable PolyHIPEs by using microfluidics, J. Mater. Chem. B 2 (2014) 2290–2300.
[9] S. Andrieux, W. Drenckhan, C. Stubenrauch, Highly ordered biobased scaffolds: from liquid to solid foams, Polymer 126 (2017) 425–431.
[10] J. Elsing, A. Quell, W. Drenckhan, C. Stubenrauch, Monodisperse polystyrene foams via microfluidics - a novel templating route, Adv. Eng. Mater. 17 (5) (2015) 604–609.
[11] F. Dehli, L. Rebers, C. Stubenrauch, A. Southan, Higly ordered gelatin methacryloyl hydrogel foams with tunable pore sizes, Biomacromolecules 20 (7) (2019) 2666–2674.

[12] M.L. Dabrowski, M. Hamann, C. Stubenrauch, Formulation and Polymerization of foamed 1,4-BDDMA-in-Water Emulsions, RSC Advances (January 2020). Submitted for publication.
[13] M. Dabo, Analyse du comportement mécanique des mousses polymères: apport de la tomographie X et de la simulation numérique, Université des Strasbourg, PhD thesis, 2015
[14] R.G. Holdich, M.M. Dragosavac, G.T. Vladisavljević, S.R. Kosvintsev, Membrane emulsification with oscillating and stationary membranes, Ind. Eng. Chem. Res. 49 (2010) 3810–3817.
[15] S.R. Kosvintsev, G. Gasparini, R.G. Holdich, I.W. Cumming, M.T. Stillwell, Liquid–liquid membrane dispersion in a stirred cell with and without controlled shear, Ind. Eng. Chem. Res. 44 (2005) 9323–9330.
[16] M.T. Stillwell, R.G. Holdich, S.R. Kosvintsev, G. Gasparini, I.W. Cumming, Stirred cell membrane emulsification and factors influencing dispersion drop size and uniformity, Ind. Eng. Chem. Res. 46 (2007) 965–972.
[17] M.M. Dragosavac, M.N. Sovilj, S.R. Kosvintsev, R.G. Holdich, G.T. Vladisavljević, Controlled production of oil-in-water emulsions containing unrefined pumpkin seed oil using stirred cell membrane emulsification, J. Membr. Sci. 322 (2008) 178–188.
[18] G. Gasparini, S.R. Kosvintsev, M.T. Stillwell, R.G. Holdich, Preparation and characterization of PLGA particles for subcutaneous controlled drug release by membrane emulsification, Colloids Surf. B Biointerfaces 61 (2008) 199–207.
[19] E. Egidi, G. Gasparini, R.G. Holdich, G.T. Vladisavljević, S.R. Kosvintsev, Membrane emulsification using membranes of regular pore spacing: Droplet size and uniformity in the presence of surface shear, J. Membr. Sci. 323 (2008) 414–420.
[20] P.S. Silva, V.M. Starov, R.G. Holdich, Membrane emulsification: Formation of water in oil emulsions using a hydrophilic membrane, Colloid. Surf. A Pysicochem. Eng. Asp. 532 (2017) 297–304.
[21] C. Stubenrauch, A. Menner, A. Bismarck, W. Drenckhan, Emulsion and foam templating – promising routes to tailor-made porous polymers, Angew. Chem. Int. Ed. 57 (2018) 10024–10034.
[22] A. Bals, U. Kulozik, Effect of pre-heating on the foaming properties of whey protein isolate using a membrane foaming apparatus, Int. Dairy J. 13 (2003) 903–908.
[23] N. Mueller-Fischer, H. Bleuler, E.J. Windhab, Dynamically enhanced membrane foaming, Chem. Eng. Sci. 62 (2007) 4409–4419.
[24] C. Claaßen, M.H. Claaßen, V. Truffault, L. Sewald, G.E.M. Tovar, K. Borchers, A. Southan, Quantification of substitution of gelatin methacryloyl: best practice and current pitfalls, Biomacromolecules 19 (2018) 42–52.
[25] W. Drenckhan, D. Langevin, Monodisperse foams in one to three dimensions, Curr. Opin. Colloid Interface Sci. 15 (2010) 341–358.
[26] P.B. Umbanhowar, V. Prasad, D.A. Weitz, Monodisperse Emulsion Generation via Drop Break Off in a Coflowing Stream, Langmuir 16 (2) (2000) 347–351.
[27] Micropore Technologies, Micropore LDC-1 User Manual, Version 3.00, March 2018.
[28] K.L. Thompson, S.P. Armes, D.W. York, Preparation of pickering emulsions and colloidosomes with relatively narrow size distributions by stirred cell membrane emulsification, Langmuir 27 (2011) 2357–2363.
[29] M.M. Dragosavac, G.T. Vladisavljević, R.G. Holdich, M.T. Stillwell, Production of porous silica microparticles by membrane emulsification, Langmuir 28 (2012) 134–143.
[30] E. Piacentini, L. Giorno, M.M. Dragosavac, G.T. Vladisavljević, R.G. Holdich, Microencapsulation of oil droplets using cold water fish gelatine/gum arabic complex coacervation by membrane emulsification, Food Res. Int. 53 (2013) 362–372.
[31] J. Santos, G.T. Vladisavljević, R.G. Holdich, M.M. Dragosavac, J. Muñoz, Controlled production of eco-friendly emulsions using direct and premix membrane emulsification, Chem. Eng. Res. Des. 98 (2015) 59–69.
[32] A. Imbrogno, M.M. Dragosavac, E. Piacentini, G.T. Vladisavljević, R.G. Holdich, L. Giorno, Polycaprolactone multicore-matrix particle for the simultaneous encapsulation of hydrophilic and hydrophobic compounds produced by membrane emulsification and solvent diffusion processes, Colloid. Surf. B: Biointerfaces 135 (2015) 116–125.
[33] L.G. Phillips, S.T. Yang, W. Schulman, J.E. Kinsella, Effects of lysozyme, clupeine, and sucrose on the foaming properties of whey protein isolate and β-lactoglobulin, J. Food Sci. 53 (3) (1989) 743–747.
[34] E.C. Needs, A. Huitson, The contribution of milk serum proteins on the development of whipped cream structure, Food Struct. 10 (4) (1991) 353–360.
[35] C.W. Pernell, E.A. Foegeding, C.R. Daubert, Measurement of the yield stress of protein foams by Vane Rheometry, J. Food Sci. 65 (1) (2000) 110–114.
[36] A.K. Smith, H.D. Goff, Y. Kakuda, Microstructure and rheological properties of whipped cream as affected by heat treatment and addition of stabilizer, Int. Dairy J. 10 (2000) 295–301.
[37] W. Drenckhan, A. Saint-Jalmes, The science of foaming, Adv. Colloid Interface Sci. 222 (2015) 228–259.
[38] E. Hoch, T. Hirth, G.E.M. Tovar, K. Borchers, Chemical tailoring of gelatin to adjust its chemical and physical properties for functional bioprinting, J. Mater. Chem. B 1 (41) (2013) 5675–5685.
[39] E. Hoch, C. Schuh, T. Hirth, G.E.M. Tovar, K. Borchers, Stiff gelatin hydrogels can Be photo-chemically synthesized from low viscous gelatin solutions using molecularly functionalized gelatin with a high degree of methacrylation, J. Mater. Sci.: Mater. Med. 23 (11) (2012) 2607–2617.
[40] F. Schüler, D. Schamel, A. Salonen, W. Drenckhan, M.D. Gilchrist, C. Stubenrauch, Synthese von makroporösen Polystyrol durch Polymerisation geschäumter Emulsionen, Angew. Chem. 124 (2012) 2256–2260.
[41] J. Elsing, A. Quell, C. Stubenrauch, Toward functionally graded polymer foams using microfluidics, Adv. Eng. Mater. 19 (2017) 1700195.
[42] J. Elsing, T. Stefanov, M.D. Gilchrist, C. Stubenrauch, Monodisperse polystyrene foams via polymerization of foamed emulsions: structure and mechanical properties, Phys. Chem. Chem. Phys. 19 (2017) 5477–5485.
[43] https://www.micropore.co.uk/micropore-range-407000.html (last checked 16.01.2020).
[44] M. Costantini, C. Colosi, P. Mozetic, J. Jaroszewicz, A. Tosato, A. Rainer, M. Trombetta, W. Swieszkowski, M. Dentini, A. Barbetta, Correlation between porous texture and cell seeding efficiency of gas foaming and microfluidic foaming scaffolds, Mat. Sci. Eng. C 62 (2016) 668–677.