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Production of monodispersed food O/W emulsions using Shirasu-porous-glass (SPG) membrane emulsification

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Abstract

The O/W emulsions containing Tween 80 dissolved in demineralized water as the continuous phase and rapeseed oil as the dispersed phase were prepared using different emulsification methods. The influence of operating conditions on droplet size distribution (DSD) was discussed and compared.

1. Introduction

Membrane emulsification (ME) is a new emulsification technology for making monodispersed emulsions over a wide spectrum of mean droplet sizes, ranging from cca. 0.5 μm to several tens of μm [1]. ME involves the permeation of pure dispersed phase through a porous membrane into moving continuous phase (direct ME) or the passage of previously prepared pre-emulsion through a membrane (premix ME [2]). In direct ME, small droplets are directly formed at the membrane/continuous phase interface and detached from the pore openings by the shear stress in continuous phase generated by stirring or flowing (Fig. 1a). The membrane must not be wetted with the continuous phase, i.e. O/W emulsions are prepared by a hydrophilic membrane and W/O emulsions by a hydrophobic membrane. In premix ME, small uniform droplets are formed by the disruption of large polydispersed droplets of a premix inside the pores (Figs. 1b and 1c). If the membrane wall is wetted with the continuous phase, droplet disruption is followed by phase inversion, i.e. a fine W/O emulsion is produced from an O/W premix and *vice versa*. The droplets prepared by direct ME are more uniform, but on the account of smaller membrane productivity.

ME holds several advantages over conventional emulsification methods based on high-pressure and rotor-stator systems: (a) droplet uniformity is much better; (b) mean droplet size can be adjusted over a much wider range, which is of special importance in the preparation of multiple emulsions; (c) the required mechanical stress is much smaller, which minimize the mechanical degradation of shear-sensitive ingredients, such as starch and proteins.

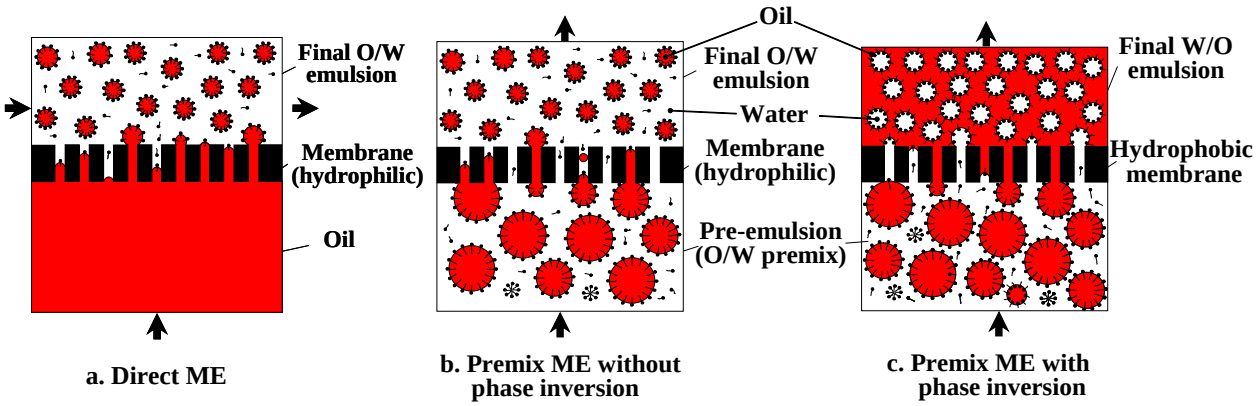


Fig. 1. Preparation of fine emulsions using different ME procedures

Nowadays, ME is mostly used for the small-scale production of highly advanced products (droplets or particles) with precisely controlled properties for functional food, electronics, medical care, analytical proposes, etc. These applications include the preparation of multiple emulsions for drug delivery systems (DDS) [3], metal solder particles for surface mount technology [4], solid microcarriers for the encapsulation of a nutrient or drug [5], silica powder for HPLC [3], monodispersed polymer microspheres as packings for analytical columns, carriers of enzymes, spacers for liquid crystal displays, etc [3]. A promising large-scale application of ME in food industry is the production of low-calorie spreads, dressings and salads, such as low-calorie margarine (W/O emulsion) containing up to 75 vol. % of dispersed water phase [3] or O/W/O spreads [6]. The other applications include the development of emulsion gel foods for the elderly generation, the preparation of new O/W/O/W emulsions for the purpose of enclosing flavor-enhancing components, the preparation of food W/O/W emulsions containing anthocyanin in the inner aqueous phase, etc.

Shirasu porous glass (SPG) membrane developed by Nakashima and Shimizu [7] was used in the majority of the above mentioned ME applications. This membrane is manufactured by the phase separation of CaO-Al_2O_3-B_2O_3-SiO_2 type glass synthesized from a Japanese volcanic ash called Shirasu. SPG membranes possess uniform interconnected micropores and the mean pore size can be varied over a wide range of 0.05-30 μm. The additional advantage is that the surface wettability can be easily changed by reaction with organic silanes or by surface treatment with a silicone resin. Therefore, SPG membrane is suitable for the production of both O/W and W/O emulsions. Other porous materials have been also investigated for use in ME, such as polymeric membranes [8], ceramic α-Al_2O_3 and Zr_2O_3 membranes [9], stainless steel plates with laser-drilled holes, microengineered silicon microsieves, etc.

The aim of this study is to compare droplet size distribution (DSD) of O/W emulsions prepared using SPG membranes, ceramic α-Al_2O_3 membranes and the microfluidizer® using the same emulsion formulation. The main factors influencing mean droplet size and DSD have been also briefly discussed.

2. Experimental

O/W emulsions were prepared using vegetable (rapeseed) oil (Floreal GmbH) with a viscosity of 58 mPa s as the dispersed phase and 2 wt. % Tween 80 (Merck GmbH) dissolved in demineralized water as the continuous phase.

The SPG membranes (10 mm outer diameter × 0.7 mm wall thickness) were supplied from SPG Technology Co., Ltd (Sadowara, Japan) with a mean pore size in the range of 0.4-6.6 μm and a wall porosity between 0.53 and 0.60. The effective membrane area was 31.3 cm^2. The Al_2O_3 membrane tubes were supplied from Membraflow GmbH & Co. KG (Aalen, Germany) with a mean pore size of 1.4 and 0.5 μm. These membranes are composed of thin skin layer (with a porosity of 0.35), supported by a porous substructure (2 mm thickness).

The direct ME system shown in Fig. 1a was used. The continuous phase was recirculated inside the membrane tube and the dispersed phase was fed at the outer side using a pressure vessel. The weight of dispersed phase permeated through the membrane was measured by a balance on which the pressure vessel rested. In some experiments, the microfluidizer® (Microfluidics Corp., Newton, USA) was used for emulsification. DSD for all samples was measured by a Coulter LS 230 particle size analyser using PIDS technology, which allowed the detection of droplets in the wide range of 0.04-2000 μm.

3. Results and discussion

As shown in Fig. 2, the emulsion droplets produced by SPG membrane emulsification were more uniform than that prepared by the microfluidizer®. On the other hand, microfluidization is an indispensable method for making very fine emulsions. E.g., using two consecutive passes through the homogenizing valve at 1100 bar, a mean droplet size of only 0.085 μm can be obtained. In this work, droplet uniformity is expressed as the span of DSD: span = $(d_{90}-d_{10})/d_{50}$, where d_{x0} is the diameter corresponding to x0 vol. % on a relative cumulative DSD curve. The span of DSD was higher for the droplets produced using α-Al_2O_3 than SPG membrane. However, the obtained spans of DSD of 0.51-0.59 for α-Al_2O_3 membrane at the dispersed phase flux till 9 l m^{-2} h^{-1} were smaller than 0.83, found by Williams et al. [10] for an 0.5 μm α-Al_2O_3 membrane.

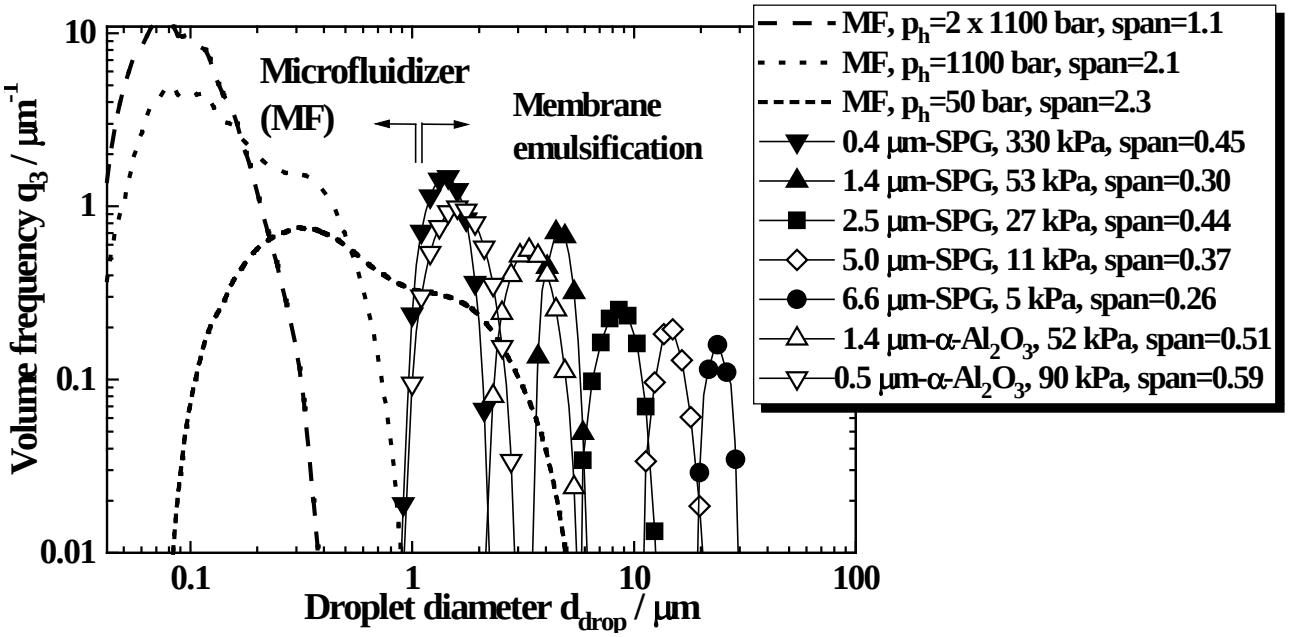


Fig. 2. Influence of emulsification method on DSD (dispersed phase content, $\varphi \approx 1$ vol. %, shear stress at the membrane surface, σ_w = 8 Pa, $\Delta p_{tm}=1.1\text{-}2.2 p_{cap}$)

In order to achieve the permeation of oil through the membrane, the transmembrane pressure must be higher than the capillary pressure given by the Laplace equation: $p_{cap} = 4\gamma\cos\theta/d_p$, where γ is the equilibrium interfacial tension between the continuous and dispersed phase (in this study $\gamma = 8 \times 10^{-3}$ N/m), d_p is the mean pore size, and θ is the contact angle between the dispersed phase and membrane surface. The DSD curves presented in Fig. 2 are obtained at the transmembrane pressure 1.1-2.2 times larger than the capillary pressure, p_{cap}.

The mean droplet size linearly increased with increasing the mean pore size, and the mean proportionality constant was 3.5 for the SPG membrane at the transmembrane to capillary pressure ratio of 1.1-1.5 (Fig. 3). The mean droplet to mean pore size ratio of 3.5 found here is similar to 3.25 reported by Nakashima et al. [1]. Fig. 4 demonstrates that the ratio of mean droplet to mean pore size increased with increasing the $\Delta p_{tm}/p_{cap}$ ratio, both for the SPG and α-Al_2O_3 membrane. However, at $\Delta p_{tm}/p_{cap} < 2$, the mean droplet size was nearly constant. The smaller $d_{3,2}/d_p$ ratio was found for the α-Al_2O_3 than for SPG membrane. The influence of transmembrane pressure on the mean droplet size was less significant at the higher wall shear stress. Accordingly, at the higher pressure ratios ($\Delta p_{tm}/p_{cap} > 4$), the shear stress in continuous phase must be high enough to prepare a monodispersed emulsion and to get a small mean droplet size. On the other hand, at $\Delta p_{tm}/p_{cap} < 2$, the mean droplet size is only slightly

affected by the wall shear stress and therefore, it is unnecessary to apply high continuous phase flow rates under such conditions.

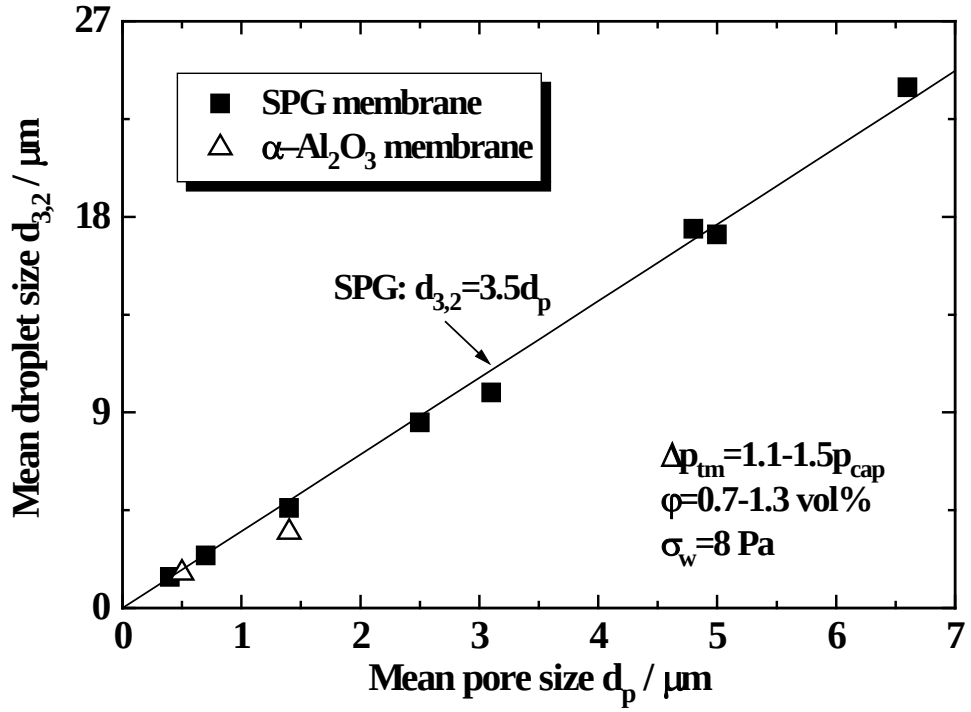


Fig. 3. Mean pore size vs. mean droplet size for SPG and α-Al_2O_3 membrane

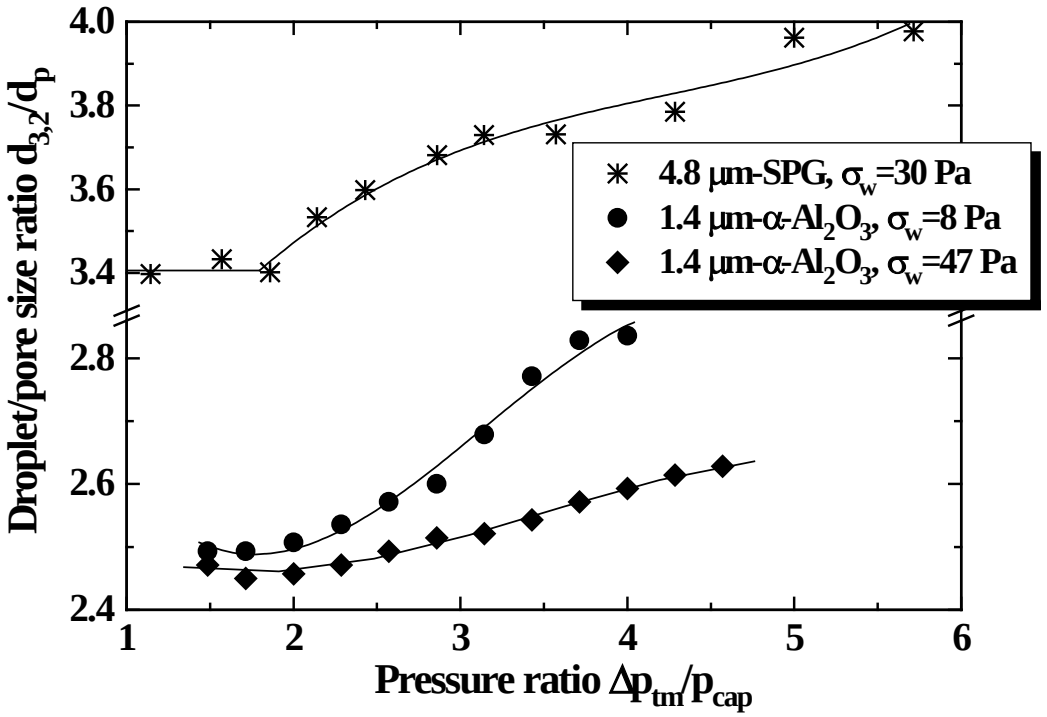


Fig. 4. The variation of mean droplet/ pore size ratio with pressure ratio.

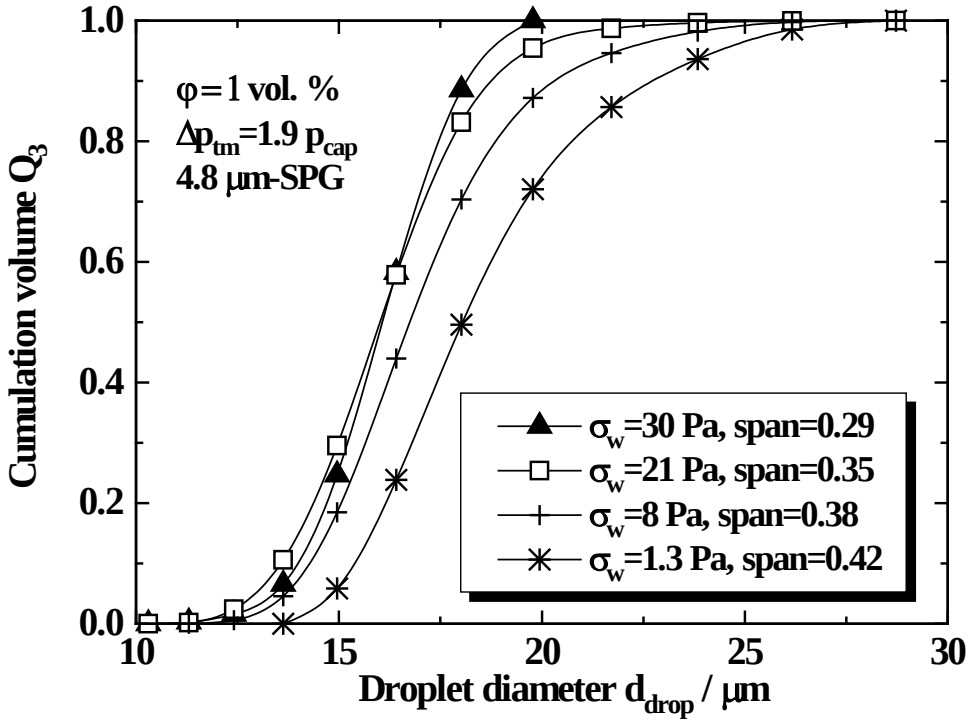


Fig. 5. Influence of wall shear stress on DSD

The wall shear stress has a considerable influence on DSD, as shown in Fig. 5. The wall shear stress was calculated using the general expression:

$$\sigma_w = \frac{d_i}{4}\frac{\Delta p_{fr}}{L} \qquad (1)$$

where d_i is the inner diameter of membrane tube and Δp_{fr} is the pressure drop for overcoming friction resistance in the membrane tube over a length L. In the special case of laminar flow inside the membrane tube ($Re_c < 2300$), Eq. (1) is simplified to: $\sigma_w = 8\mu_c v_c/d_i$, where v_c is the mean velocity of continuous phase inside the membrane tube and μ_c is the continuous phase viscosity. In the case of turbulent flow inside the membrane tube, Eq. (1) has the following form:

$$\sigma_w = \frac{\rho_c v_c^2}{8}\lambda$$

where ρ_c is the continuous phase density and λ is the Moody friction factor, which is at $2{,}500 < Re_c < 100{,}000$ given by the Blasius equation:

$$\lambda = \frac{0.3164}{Re_c^{0.25}}$$

As shown in Fig. 5, more uniform droplets are formed at the higher wall shear stress. The span of DSD decreased by about 30 % as the wall shear stress

increased from 1.3 to 30 Pa. In addition to better uniformity, the droplets are also smaller at the higher wall shear stress, which is also clear from Fig. 4.

4. Conclusion

The microporous membranes (SPG and α-Al_2O_3) were successfully used to produce O/W emulsions with remarkably narrow DSD curves (span = 0.26-0.59). At the same pore size and experimental conditions, SPG membranes gave better droplet uniformity than α-Al_2O_3 membrane. For making O/W emulsions with very small mean droplet size, the microfluidizer® is very useful device but the obtained span of DSD was in the range of 0.9-2.7. The mean droplet size primarily depended on the mean pore size ($d_{3,2} = 3.5d_p$), but it could by finely adjusted by the magnitude of flow parameters, such as transmembrane pressure and wall shear stress.

5. Acknowledgement

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