Technical paper

Preparation of Corn Oil/Water and Water/Corn Oil Emulsions Using PTFE Membranes

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PTFE (polytetrafluoroethylene) membrane filters were tested for preparing corn oil emulsions by the membrane emulsification method using a pre-emulsified emulsion. A hydrophilic PTFE membrane was used to prepare an O/W emulsion without any disturbance of the continuous phase. A W/O emulsion was prepared with a hydrophobic membrane filter in the same way. The higher the flux of the pre-emulsified large particle emulsion via the membrane was, the higher the monodispersibility of the membrane emulsified emulsion became. There was no limit to the emulsifying pressure or the emulsifying rate under the conditions tested. The mean particle diameters of the O/W and W/O emulsions were ca. 3 times the mean pore size of the membrane used.

Keywords: membrane emulsification, pre-emulsified emulsion, PTFE membrane, emulsifying rate, monodispersibility, stability

The membrane emulsification method entails passing the oil or water phase directly through micropores in a porous membrane by applying pressure and dispersing it into a continuous phase as fine particles (Nakashima & Shimizu, 1993). The particle diameter distribution of the emulsions prepared by this method is analogous to the pore size distribution of the membranes used (Nakashima & Shimizu, 1993). This means that monodispersed emulsions could be prepared if porous membranes of uniform pore size were available (Kawakatsu *et al.*, 1996). It has also been mentioned that the membrane emulsification method can be used to prepare emulsions without high mechanical stress at a lower energy input compared with the emulsification methods (Schubert, 1997). One of the disadvantages of this method was a low emulsifying rate; this was improved recently by passing a previously emulsified emulsion of rough particle diameter through the porous membrane instead of the direct passage of the oil or water phase (Suzuki *et al.*, 1994; 1996). There was no limit to the emulsifying rate of the method, and the particle diameter of the emulsions decreased with the increase in applied pressure or flux of the pre-emulsified emulsion through the membrane (Suzuki *et al.*, 1996).

The membrane emulsification method requires a hydrophilic membrane when the continuous phase of emulsion is water or water with emulsifying agents, and a hydrophobic membrane for the continuous phase of oil. A porous glass membrane, which has been used in most of the studies on the membrane emulsification method, is basically hydrophilic due to the silanol groups, and is useful for preparing O/W emulsions (Nakashima & Shimizu, 1993). However, the glass membrane has not been adapted to cleaning under alkaline conditions, and the chemical modifications for making it hydrophobic are not acceptable for preparing W/O food

emulsions (Katoh, 1995). For this reason, we have tested several hydrophilic and hydrophobic membrane filters applicable to preparing O/W and W/O emulsions of corn oil by the membrane emulsification method with preliminary emulsification. Among the membrane filters tested, we have found the PTFE (polytetrafluoroethylene) membrane filter to be the most desirable, with its high chemical and heat resistances, though the pore size distribution is somewhat wider than that of the glass membrane. We can obtain both hydrophilic and hydrophobic PTFE membrane filters easily on the market.

The objective of this paper was to clarify the usefulness of the PTFE membranes for preparing O/W and W/O food emulsions made from a vegetable oil by the membrane emulsification method combined with preliminary emulsification. The effects of the preliminary emulsifying conditions and emulsifying pressure or permeating rate of the pre-emulsified emulsion through the PTFE membrane on the mean particle diameter and the particle diameter distribution of the emulsions prepared were also investigated.

Materials and Methods

PTFE membrane filters The properties of the sheet type PTFE membrane filters (Advantec Toyo, Ltd., Tokyo) used in this study were in Table I, where D_m is the mean pore size and δ is the thickness. The values of D_m and δ are from the manufacturer's catalogue, and the D_m^* values are the mean pore sizes measured for one lot of the membranes (Fig. 1). The values plotted in Fig. 1 were courtesy of the producer. Though the pore size distributions of the membranes were slightly wider than those of the porous glass membranes (Nakashima & Shimizu, 1993) and the mean pore sizes were slightly different from the catalogue values, the pore size distributions of the PTFE membranes were still fairly narrow,

Table 1. The properties of the sheet type PTFE membrane filters.

Type (Code)	Size (mm)	D_m (D_m^*) (μm)	δ (μm)
Hydrophilic (H100A047A)	47	1.0 (0.82)	35
Hydrophobic (T100A047A)	47	1.0 (1.05)	75

Fig. 1. Pore size distributions of the PTFE membranes used in this study. ○ Hydrophilic PTFE membrane, ● Hydrophobic PTFE membrane.

as shown in Fig. 1.

Preparation of membrane-emulsified O/W and W/O emulsions Corn salad oil (Ajinomoto Co., Inc., Tokyo) was used for the oil phase and distilled water for the water phase. The emulsifying agents used in the oil phase and water phase were a hexaglycerol polyricinoleate (CR-500, HLB<1) and a decaglycerol monolaurate (ML-750, HLB=15), respectively. Both CR-500 and ML-750 were the products of Sakamoto Yakuhin Kogyo Co., Ltd., Osaka. The concentration of each emulsifying agent was fixed at 2.0 wt% in the oil phase or the water phase. Two emulsifying agents were used for preparing both O/W and W/O emulsions.

The diagram of the membrane emulsifying apparatus used in this study is shown in Fig. 2. This apparatus was used to prepare the membrane-emulsified emulsion just by passing the entire pre-emulsified emulsion through the membrane without any circulation or stirring of the continuous phase. Thus, the dispersed phase concentration of the emulsion was almost the same as that of the pre-emulsified emulsion. For preparing the O/W emulsion, the hydrophilic PTFE membrane was used, and the hydrophobic membrane was used for the W/O emulsion. The membrane was dipped in the continuous phase and evacuated at ca. 10 kPa-abs for 5 min to make sure that the membrane was thoroughly wet with the continuous phase before fitting the membrane in the apparatus. In the preliminary emulsifying process, we prepared the same type of emulsion that we wanted to prepare in the membrane emulsifying process. The particle diameter of the pre-emulsified emulsions was changed by regulating the mixing rate and time of the mixer (Homomixer-HV-M, Tokushukikakogyo, Osaka). The pre-emulsified emulsion was then degassed at about 60 Torr (8 kPa-abs) in a vacuum chamber. The pre-emulsified large particle emulsion was then poured into the apparatus followed by applying pressure. The

permeating flux or emulsifying rate was controlled by regulating the pressure. Though the membrane emulsification method combined with the preliminary emulsification prepares O/W and W/O emulsions of a wide range of the dispersed phase concentration, the dispersed phase concentrations in the final O/W and W/O emulsions tested were 30 wt% and 20 wt%, respectively, in this study. These values correspond nearly to the dispersed phase concentration of common O/W and W/O emulsions such as whipped cream and margarine.

Measurement of particle size distribution The emulsion was diluted with the liquid of the continuous phase, i.e., distilled water or corn oil, and then the particle size distribution was analyzed by an image analyzer (Olympus SP-500, Tokyo).

Results and Discussion

Membrane emulsification by passing the oil phase or the water phase directly through the PTFE membrane was almost impossible. Even if a small amount of emulsion was obtained at very low permeating rate, the emulsion properties could not be measured because of the extremely low stability. However, we obtained both O/W and W/O emulsions of stable and of narrow particle diameter distribution at high permeating flux via the membrane by passing the pre-emulsified emulsion through the membrane. The emulsifying characteristics are described as follows.

Influence of pre-emulsifying conditions on the permeating flux of the pre-emulsified emulsions The permeating flux of the pre-emulsified emulsion through the membrane increased almost linearly with an increase in the pressure applied. In addition, the flux was also affected by the pre-emulsifying conditions as shown in Fig. 3. The flux was indicated as the permeating volume per hour instead of per second in the figure for easy understanding of the production rate. The lower the agitation speed in the pre-emulsification process was, the higher the permeating flux of the pre-emulsified emulsion became through the membrane for both of the

Fig. 2. Schematic diagram of the membrane emulsifying apparatus used in this study.

O/W and W/O emulsions. The reason is considered to be that the deforming energy for larger liquid particles is lower than that for smaller particles, when the liquid particles pass through the narrow channels of the membrane, because the

Laplace pressure of larger particles is lower than that of smaller particles (Dickinson & Stainsby, 1988). The experimental results showed that it is possible to prepare several tons of O/W or W/O emulsions per square meter of the

Fig. 3. Influence of pressure and pre-emulsifying conditions on the permeating flux of the pre-emulsified O/W or W/O emulsions via the hydrophilic or hydrophobic PTFE membrane used. (A) Pre-emulsified O/W emulsions, (B) Pre-emulsified W/O emulsions.

Fig. 4. Influence of pressure and pre-emulsifying conditions on the mean particle diameter of the membrane-emulsified O/W and W/O emulsions. (A) O/W emulsions, (B) W/O emulsions.

Fig. 5. Influence of pressure and pre-emulsifying conditions on the variance, D , of particle diameter distribution of the membrane-emulsified O/W and W/O emulsions. (A) O/W emulsions, (B) W/O emulsions. $D = \left[\sum_{i=1}^N Dp_i^2 - \left(\frac{\sum_{i=1}^N Dp_i}{N} \right)^2 \right] / N$

Fig. 6. Comparison of the particle diameter distribution of the freshly prepared O/W emulsion with that of the emulsion which was kept at room temperature for 14 days (Pre-emulsifying conditions: 5000 rpm, 5 min. Pressure for membrane emulsification: 0.7 MPa) ● 0 day, ○ After 14 days.

membrane per hour.

Influence of emulsifying pressure on mean particle diameter When the emulsifying pressure or the permeating flux of the pre-emulsified emulsion was low, the mean particle diameter of the membrane-emulsified emulsion increased. However, the mean particle diameter decreases as higher pressure was applied, and values for both the O/W and W/O emulsions reached about threefold the measured values of the mean pore size of the membranes in this study as shown in Fig. 4. Though the ratio of the mean particle diameter to the mean pore size of the membrane was smaller than 3.25 (Nakashima & Shimizu, 1993) or 5.0 (Katoh *et al.*, 1995) obtained by the method in which the dispersed phase was passed directly through the membrane, the value was slightly larger than that obtained in our previous study (Suzuki *et al.*, 1996). The results probably depended on the properties of the PTFE membranes used, such as thickness, pore size distribution, surface properties and mechanical strength of the membrane. The analyzing method of the particle diameter distribution also possibly influenced the results.

Influence of pressure on particle diameter distribution The pressure on the pre-emulsified emulsions for passing through the membrane affected the particle diameter distribution of the emulsions prepared, as shown in Fig. 5. The variance D of the particle diameter distribution in the ordinate is defined as

$$D = \left[\sum_{i=1}^N Dp_i^2 - \left\{ \left(\sum_{i=1}^N Dp_i \right)^2 / N \right\} \right] / N$$

where Dp_i is the diameter of the i -th sample number and N is the total sample number. When the pressure or the permeating flux was low, the distribution was also affected by the pre-emulsifying conditions. However, an almost constant value of the distributions was obtained at higher pressures. This means that a higher pressure or higher permeating flux produced emulsions with better monodispersibility, regard-

less of the pre-emulsifying conditions. Because of the wider pore size distribution of the PTFE membrane filters compared with that of a porous glass membrane (Nakashima & Shimizu, 1993), and probably because of the change in the pore size due to deformation of the membrane with pressure, the monodispersibility of the emulsions prepared in this study was slightly lower than those prepared with the glass membrane (Suzuki *et al.*, 1996). However, the O/W and W/O emulsions prepared in this study were very stable, and no appreciable change in the particle diameter distribution was observed over two weeks or longer, as shown in Fig. 6 as one example. This study made it clear that the PTFE membrane emulsification with preliminary emulsification is characterized by the preparation of stable O/W and W/O emulsions with a narrow particle distribution at a high rate.

Conclusions

The PTFE membrane emulsification with preliminary emulsification for preparing corn oil-water emulsions was tested. The method prepared O/W or W/O emulsions with a narrow particle diameter distribution using a hydrophilic or hydrophobic PTFE membrane filter. The higher the flux of the pre-emulsified emulsion via the membrane, the higher the monodispersibility of the membrane emulsified emulsion was. There was no limit to the emulsifying pressure or emulsifying rate under the conditions tested.

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