Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Synthesis of Ceramic Microfiltration Membranes for Oil/Water Separation

Sang H. Hyun[a]; Gye T. Kim[a]
[a] DEPARTMENT OF CERAMIC ENGINEERING, COLLEGE OF ENGINEERING YONSEI UNIVERSITY SEOUL, SOUTH KOREA

To cite this Article Hyun, Sang H. and Kim, Gye T.(1997) 'Synthesis of Ceramic Microfiltration Membranes for Oil/Water Separation', Separation Science and Technology, 32: 18, 2927 — 2943
To link to this Article: DOI: 10.1080/01496399708000788
URL: http://dx.doi.org/10.1080/01496399708000788

SEPARATION SCIENCE AND TECHNOLOGY, **32**(18), pp. 2927–2943, 1997

Synthesis of Ceramic Microfiltration Membranes for Oil/Water Separation

SANG H. HYUN* and GYE T. KIM
DEPARTMENT OF CERAMIC ENGINEERING
COLLEGE OF ENGINEERING
YONSEI UNIVERSITY
SEOUL 120-749, SOUTH KOREA

ABSTRACT

Alumina and zirconia composite membranes without defects for oil/water separation have been produced by the reverse dip-drawing technique. The thickness (5–15 μm) and the uniformity of the top layer could be appropriately controlled by adjusting process variables such as the slurry concentration and the flow rate of the slurry. The effective average pore sizes of alumina and zirconia top-layers are 0.16 μm and less than 0.07 μm, respectively. The composite membranes are found to be very effective for removing oil from o/w emulsions.

Key Words. Zirconia composite membrane; Alumina composite membrane; Reverse dip-drawing technique; Microfiltration; Oil/water separation

INTRODUCTION

Industrial growth has accelerated the emission of various oily wastes from such sources as petrochemical and metallurgical industries, transportation, and domestic sewage. These oily wastes are one of the major pollutants of the aquatic environment. Special attention has been focused on the discharge of wastewater and oily water, and its regulatory restriction has become more strict. Oil/water separation processes using polymeric/

* To whom correspondence should be addressed.

inorganic membranes have been proposed as effective and cost-competitive alternatives to conventional oil removal technologies (1–4), and have also been widely applied to meet the restrictive legal requirements. At present, however, the commercial use of membranes in wastewater treatment is limited because of their low efficiency as well as their high capital and operating costs (5). In recent years the use of ceramic membranes instead of polymeric membranes (6–11) has generated continued interest because their high chemical, mechanical, thermal, and biological stabilities are required for harsh operational conditions (10, 11). The key to the successful application of ceramic membranes in oil/water separation lies in the fabrication of ceramic membranes with larger throughput (flux) and high selectivity. Lipp et al. (2) obtained an oil separation efficiency from oil/water emulsion above 96.2% by using organic membranes, but the long-term viability of their membrane system was uncertain. On the other hand, Koltuniewicz et al. (6) claimed that the performance of zirconia membranes was superior in both oil separation efficiency and permeation flux to organic (polysulfone) membrane with the same pore size (0.1 μm) for the separation of oil-in-water emulsions. Also, Bhave and Fleming (9) suggested that although the permeate flux through an alumina membrane with a pore size of 0.2 μm had a somewhat low value of 27.2 $L/m^2{\cdot}h$, microporous alumina membranes were suitable for the removal of oily contaminants. However, oil/water separation technology using ceramic membranes is still in the developmental stage. For commercial applications of this technology, much basic research on manufacturing techniques and costs, microstructural properties, filtration efficiencies, etc. should be done.

The objective of the present study is to assess the oil/water separation efficiency of zirconia and alumina composite membranes synthesized by the reverse dip-drawing technique. The synthetic membranes were characterized by analyzing their microstructural variations with synthetic conditions and their microfiltration behaviors for oil-in-water-type emulsions.

EXPERIMENTAL PROCEDURE

Synthesis of MF Composite Membranes

α-Alumina tubes (Yootong Enterprise Co., South Korea) were used as the support (OD = 8.2 mm, ID = 6.9 mm, length = 200 mm) for preparing composite membranes. The porosity and the average pore diameter of the support were 35% and 0.8 μm, respectively. The compositions of zirconia (Dp = 0.4 μm, Tosho, Japan) and α-alumina (Dp = 0.6 μm, Showa Denko, Japan) slurries for coating microfiltration (MF) layers on the support surface are given in Table 1. In order to increase the stability and

TABLE 1
Slurry Compositions for Synthesizing Composite Membranes

Slurry	Powder (wt%)		Ethyl cellulose (wt%)	2-Propanol (wt%)
	ZrO_2	Al_2O_3		
Zirconia	8.7		2.2	89.1
Alumina		8.7	2.2	89.1
		16	2	82

the coating characteristics of the slurry, 2-propanol (special grade, Yakuri, Japan) was used as a dispersion medium and ethyl cellulose (chemical pure grade, Junsei, Japan) as a binder. Since our supports were more uniform and smoother on their inner side than on their outer side, it was desirable that the top layer (i.e., the coated layer) be formed inside the support tube. Zirconia and alumina composite membranes were fabricated by the reverse dip-drawing technique using the apparatus given in Fig. 1. The reverse dip-drawing technique which was developed in this study is

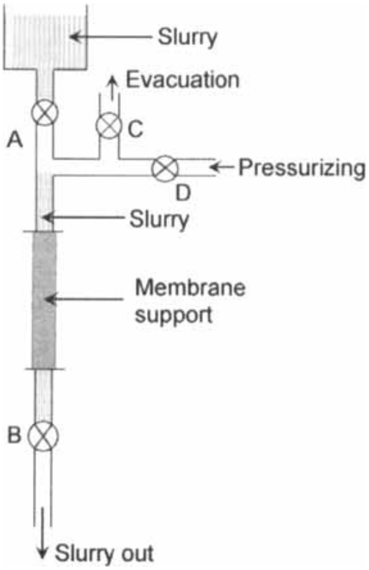

FIG. 1 Diagram of the slurry coating apparatus.

based on an idea similar to that of the dip-drawing technique for forming a uniform top-layer on the outside surface of the support by controlling the rate of drawing. For synthesizing the composite membrane, the slurry was completely filled in the support tube, followed by carefully opening Valve B to control the flow rate of the slurry instead of the rate of drawing in the dip-drawing case. If necessary, the flow rate could be controlled by Valve D for pressurizing. Before being coated with a slurry, the support tubes were cleaned in an ultrasonic 2-propanol bath for 10 minutes to keep the support clean, and then soaked in 2-propanol sufficiently to minimize the capillary force. The coated tubes were dried in air at room temperature for 1 day. The finial zirconia composite membranes were heated to 500°C at a rate of 20°C/min, followed by heating to 950°C at a rate of 30°C/min, and held there for 1 hour. Alumina composite membranes were heated to 1200°C at a rate of 4°C/min and held there for 2 hours.

Membrane Characterization

The synthetic composite membranes should be defect-free and the thickness of the top layer should be as thin and homogeneous as possible to attain high separation efficiency and permeate flux. To confirm the homogeneity of the top-layer thickness, two parts in the top layer (i.e., upper and lower regions of the membranes) were examined by SEM (Akash, SX-30E, Japan). The bubble point test of ASTM F316-86 based on the Washburn equation, $d = 4\gamma \cos \theta/\Delta P$, was adopted for detecting any defects and/or large pores in the top layer. The bubble point test was performed by filling the pores of a membrane with a wetting liquid (contact angle θ) and then applying gas pressure inside the membrane. According to the Washburn equation, the largest pore or defect diameter (d) in the top layer could be determined by observing the lowest pressure (ΔP) at which a gas bubble comes out of the other side of the membrane immersed in wetting liquid. In this work, mineral oil (Sigma, USA) with a surface tension (γ) of 34.7 dyne/cm at room temperature was used as the wetting liquid. This method was also used to estimate the average pore size of the defect-free membrane. The pore size distribution was measured by mercury porosimetry (Autopore II 9220, Micromeritics, USA).

Microfiltration

To examine the MF filtration performance of synthetic membranes, separation experiments of oil droplets from an oil-in-water emulsion were done by using the crossflow filtration apparatus shown in Fig. 2, in which a single composite membrane was installed. Oil/water emulsions were prepared by vigorously stirring the mixture of 1000 mL of deionized water,

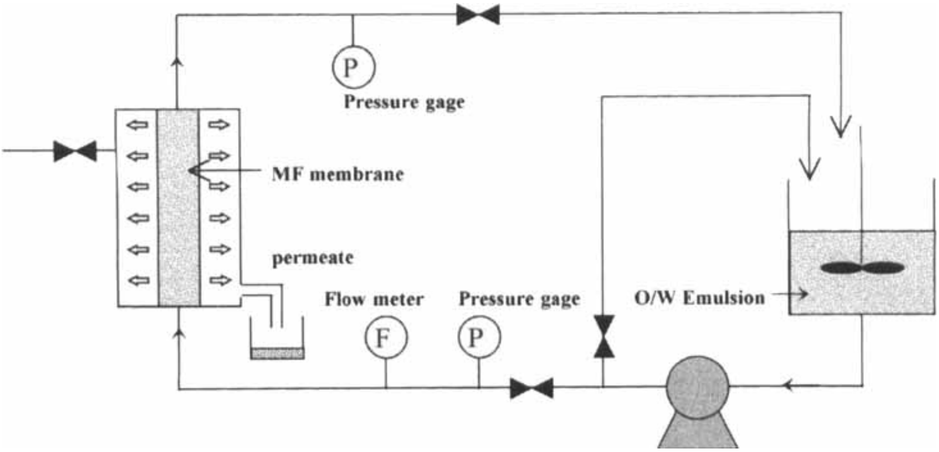

FIG. 2 Diagram of the crossflow microfiltration apparatus.

1–10 mL of kerosene (chemical pure grade, Yakuri, Japan), and 0.1–3 mL of sorbitan sesquioleate (Sigma, USA) at 6000 rpm for 1 hour. All the emulsions obtained were very stable. The size distribution of oil droplets was measured by using a centrifugal automatic particle analyzer (CAPA-300, Horiba, Japan).

The applied transmembrane pressure was in the range of 0.98–2.94 bar and the cross-flow velocity was 0.27 m/s. The permeate flux was measured by weighing the amount of the permeate, and the oil separation efficiency (SE) was calculated from the equation SE (%) = $(T_{\text{feed}} - T_{\text{permeate}})/T_{\text{feed}} \times 100$, using the total organic carbon content in the original o/w emulsion (C_{oe}) and the permeate (C_p) as determined by a total carbon analyzer (TOC-5000, Shimadzu, Japan).

RESULTS AND DISCUSSION

Top-Layer Thickness in Composite Membranes

A variety of techniques have been applied to produce a microfiltration top-layer, which is both thin and crack-free, on the surface of a porous support. As the thickness of the top-layer coated over the entire membrane becomes thinner and more uniform, the possibility of crack occurrence can be minimized. The slurry dip-drawing technique has been successfully used to coat the outside surface of a tubular-type support, while the application of this technique to coat the inside surface was found to be difficult.

In this work, therefore, the reverse dip-drawing technique described in the Experimental Section was developed and employed. Figure 3 shows SEM micrographs of the surfaces of the zirconia composite membrane prepared by coating the inside surface of the α-alumina support (length = 200 mm) with the zirconia slurry given in Table 1. As shown in Figs. 3(a) and 3(b) for fracture surfaces, the thickness of the top layer in the upper and lower regions was about 6 μm thick and uniform in both parts.

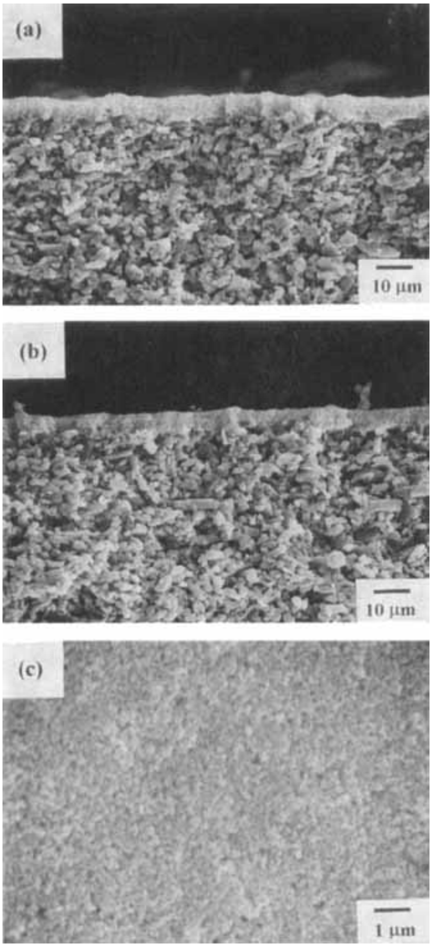

FIG. 3 SEM micrographs of zirconia membrane surfaces: (a) fracture surface of the top region, (b) fracture surface of the bottom region, and (c) surface.

It was also noted from the surface micrograph of Fig. 3(c) that there were no visible defects and that homogeneity in the surface microstructure could be obtained. The variation of the top-layer thickness with the slurry concentration at a constant flow rate of the slurry (64 mm/min) was observed for the case of the alumina composite membrane as shown in Fig. 4. When the alumina content of the slurry increased from 8.7 to 16 wt% (see Table 1), the thickness of the top layer increased from 5 to 13 μm. This result shows that the top-layer thickness can be appropriately controlled by both the slurry concentration and its viscosity. As in zirconia membranes (Fig. 3), uniformity in top-layer thickness in alumina composite membranes was also observed and known to be independent of slurry concentration. In the preliminary experiment, when the flow rate of a zirconia slurry containing 2.2 wt% ethyl cellulose and 89.1 wt% 2-propanol is about 2.4 mm/min, the thicknesses of the top layers in the upper and lower regions were about 10 and 25 μm, respectively. It was concluded that the flow rate of the slurry in the reverse dip-drawing process was required to be about 40 mm/min in order to obtain a uniform thickness

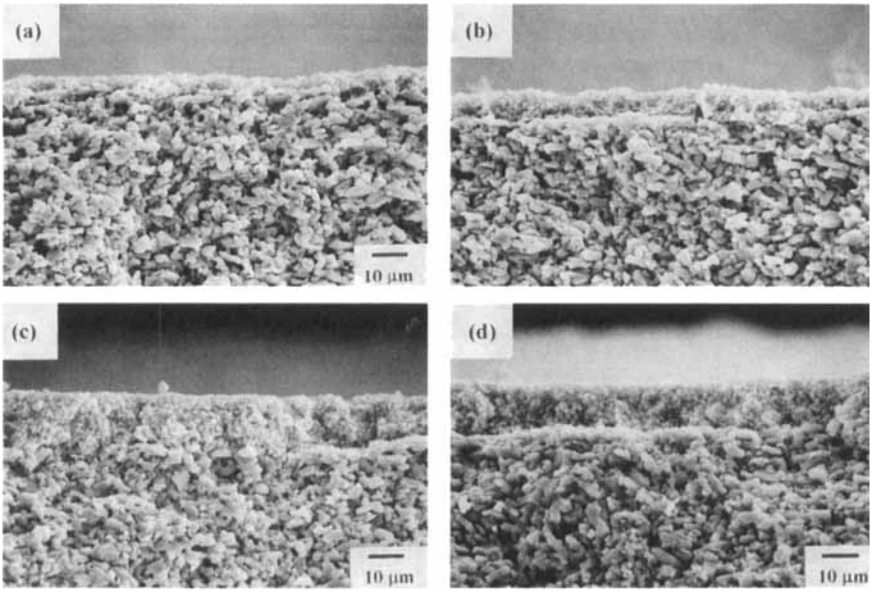

FIG. 4 SEM micrographs of fracture surfaces of alumina membranes coated with different slurry compositions. Top (a) and bottom (b) regions of the slurry with composition: alumina 8.7 wt%, ethyl cellulose 2.2 wt%, and 2-propanol 89.1 wt%. Top (c) and bottom (d) regions of the slurry with composition: alumina 16 wt%, ethyl cellulose 2 wt%, and 2-propanol 82 wt%.

over the entire composite membrane. From these results, the reverse dip-drawing technique is thought to be a desirable method for producing a thin and uniform top-layer on the inside surface of a tubular-type support.

Analysis of Pore Characteristics

In general, the pore characteristics of membranes can be evaluated as the average pore size, pore size distribution, and maximum pore/defect size. These play key roles in determining the permeability and retention property of a membrane.

Alumina Membrane

For evaluating the microfiltration capability of the composite membranes synthesized in this work, the maximum and mean pore sizes of

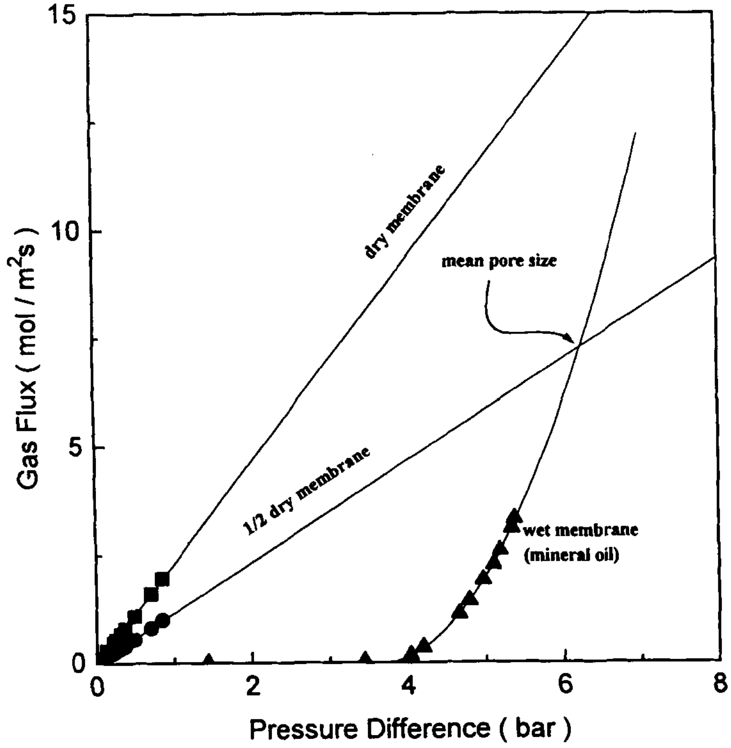

FIG. 5 Maximum and mean pore sizes of the alumina membrane as determined by the bubble point test.

the alumina composite membranes were first determined by the bubble point test (Fig. 5). The first bubble point (i.e., the largest pore size) was detected at 1.44 bar, corresponding to a pore diameter of 0.69 μm. The N_2 flux through the wet membrane was small enough not to be measured until the applied pressure reached 3.44 bar, corresponding to a pore diameter of 0.29 μm, while the flux above 3.44 bar increased rapidly as shown in Fig. 5. The average pore size of the top layer as determined by analyzing the bubble point test data in Fig. 5 was 0.16 μm, corresponding to 6.2 bar. This shows that the membrane synthesized in this work has a narrow pore size distribution because of the sharp increase in N_2 flux around the average pore diameter. Figure 6 shows the pore size distributions of alumina and zirconia composite membranes as determined by mercury porosimetry. The pore size distribution has a bimodal pattern in which the pore size distribution on the left-hand side is for the support and that on the right-hand side is for the top layer of the composite membrane. The average pore diameter of the top layer in the alumina composite membrane

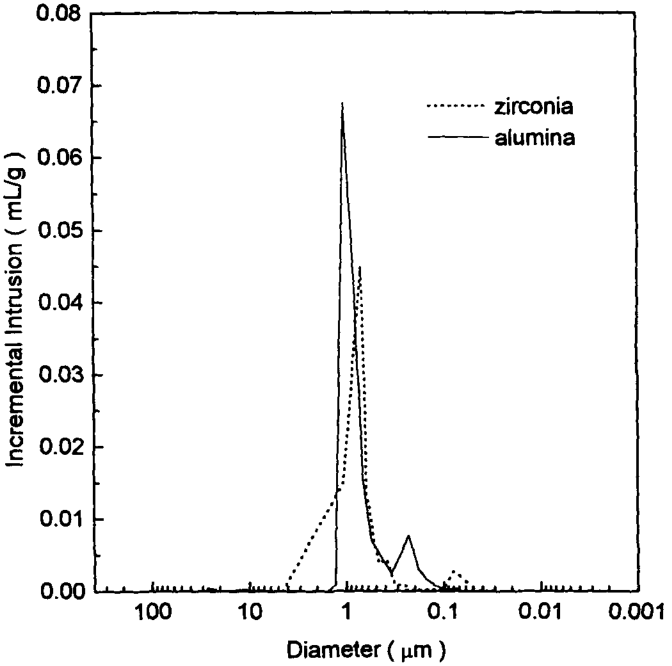

FIG. 6 Pore size distributions of zirconia and alumina composite membranes by mercury porosimetry.

was estimated to be 0.22 μm from mercury porosimetry, while it was 0.16 μm from the bubble test of Fig. 5. The difference between these values for the top layer might be due to the measurement techniques used. Venkataraman et al. (12) state that mercury porosimetry measures all pores that have at least one opening to the surface of a sample composed of composite membrane powders. In normal composite membrane applications, however, it is necessary for the substance being filtered to actually pass through the top layer, so only pores that have an opening on both sides of the top layer are important. In addition, unfortunately, mercury porosimetry cannot measure pores only in the top layer of the composite membrane while excluding the effect of support pores. On the other hand, the bubble point test method measures only pores in the top layer through which gas flows. In particular, the entire membrane top-layer in contact with the inlet fluid phase can be analyzed by this technique. Consequently, the reliable average pore diameter of our top layer useful for microfiltrations must be 0.16 μm. This value is also in good agreement with the average pore diameter (0.15 μm) of the alumina tube prepared in our laboratory by slip casting using the same alumina powders.

Zirconia Membrane

The maximum pore size of the zirconia composite membrane synthesized in this work was determined by the bubble point test, as given in Fig. 7. The first bubble point was detected at 1.6 bar, corresponding to the largest pore diameter (i.e., 0.63 μm), which is slightly smaller than that of the alumina composite membrane. Although large pores with diameters of 0.63–0.15 μm existed, the increase in N_2 flux could not be distinguished up to 6.78 bar (pore diameter of 0.15 μm) which was the pressure limit in our experimental apparatus. These results suggest that the average pore size was at least less than 0.15 μm, and also that there were few large pores which deteriorated the microfiltration efficiency. The average pore diameter of the support and of the top layer in the zirconia composite membrane as determined by mercury porosimetry (see Fig. 6) were found to be 0.7 and 0.07 μm, respectively. It is obvious from the same reasoning as in the case of the alumina composite membrane that the actual pore size of the zirconia top-layer is smaller than the 0.07 μm determined by mercury porosimetry.

Based on the above results, an alumina/zirconia composite membrane with a crack-free top-layer suitable for microfiltration can be obtained by the reverse dip-drawing technique. The maximum and mean pore sizes of the top layers in composite membranes are summarized in Table 2.

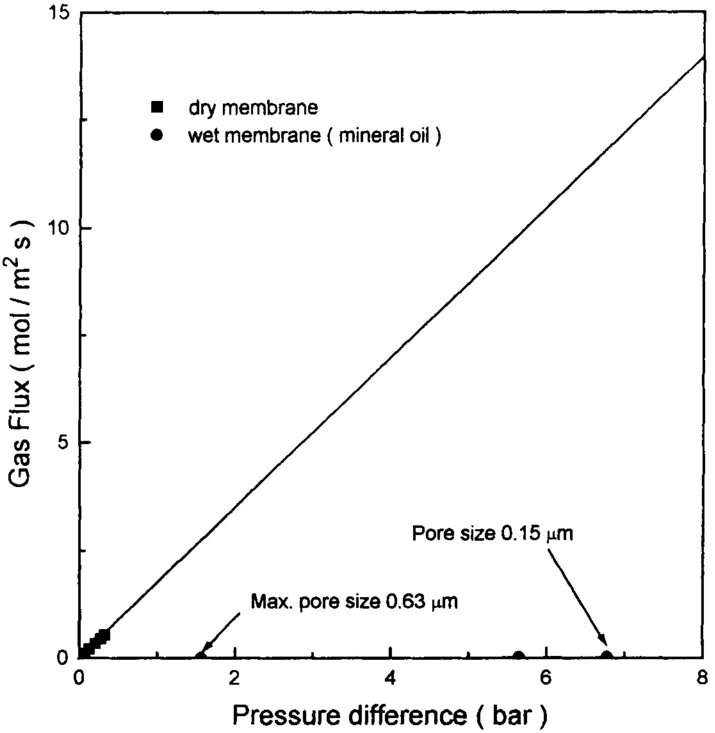

FIG. 7 Maximum pore size analysis for the zirconia membrane by the bubble point test.

TABLE 2
Pore Size Analysis of Top Layers in Composite Membranes

	Bubble point test		
Top layer	Maximum pore size (μm)	Average pore size (μm)	Mercury porosimeter, mean pore size (μm)
Zirconia	0.62	<0.15	0.07
Alumina	0.69	0.16	0.22

Microfiltration of Oil-in-Water Emulsions

For preliminary microfiltration tests of the synthetic membranes, oil separation capability from oil-in-water emulsion in the crossflow microfiltration system was examined in the conditions of transmembrane pressure of 0.98–2.94 bar, crossflow velocity of 0.27–0.55 m/s, and an emulsion concentration of 600–11,000 ppm at room temperature. It was observed that the variations of the transmembrane pressure, the crossflow velocity, and the emulsion concentration did not effect the oil separation efficiency within our experimental condition ranges. The oil separation experiment was performed in the region of relatively low emulsion concentration to minimize the concentration polarization layer effect. The transmembrane pressure was maintained at 2.94 bar in order to obtain a high permeate flux, but a crossflow velocity above 0.27 m/s was not achieved at that transmembrane pressure because of the limitations of our experimental

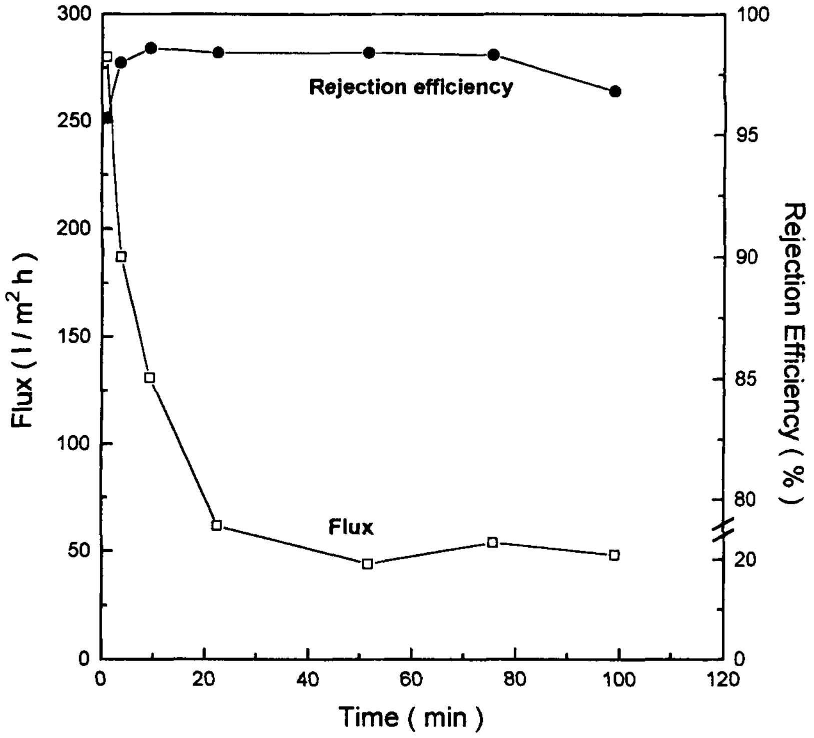

FIG. 8 Permeate flux and rejection efficiency vs operating time for the alumina membrane (transmembrane pressure 2.94 bar and crossflow velocity 0.27 m/s).

apparatus. The oil droplet size of oil-in-water emulsions used in this study was distributed over a wide range. The portion of submicron droplets was about 50%, and droplets under 0.4 μm was 23%. Figure 8 shows the variations of permeate flux and rejection (separation) efficiency through the alumina composite membrane with time at constant transmembrane pressure (2.94 bar), temperature (25°C), and crossflow velocity (0.27 m/s). The permeate flux through the alumina composite membrane decreased abruptly from 280 to 50 L/m^2·h within 20 minutes. In the early operating stage, oil droplets fill the pore entrance and create a cake on the membrane surface, which increases the flux resistance with time. After that, however, the permeate flux was found to be almost constant as time passed. This is because the rates of oil adsorption and desorption onto the membrane surface are the same. The permeate flux through the zirconia composite membrane (Fig. 9) decreased very slightly from 40 L/m^2·h in the

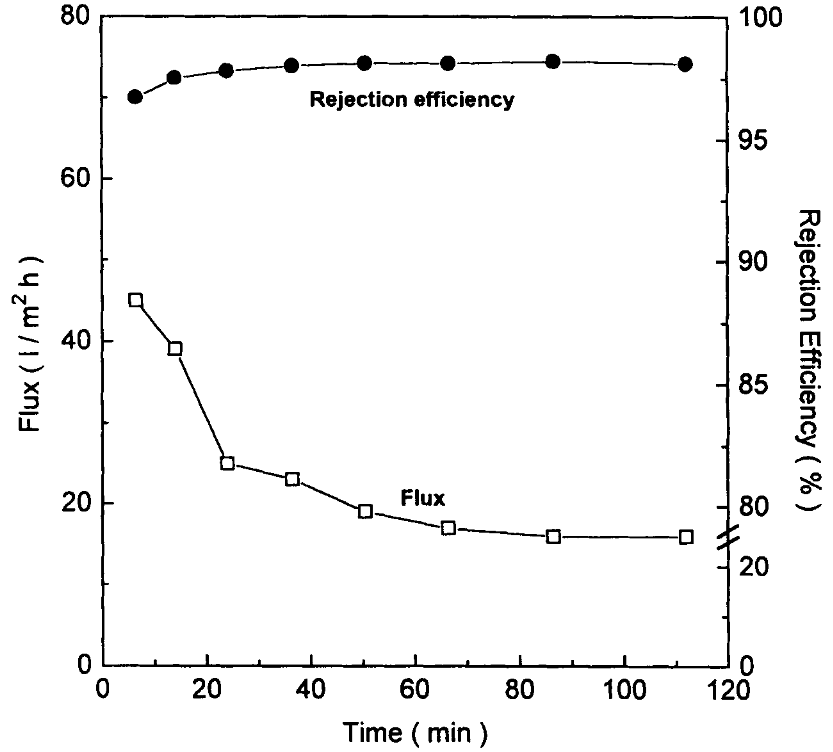

FIG. 9 Permeate flux and rejection efficiency vs operating time for the zirconia membrane (transmembrane pressure 2.94 bar and crossflow velocity 0.27 m/s).

early stages. Fouling was less pronounced for the zirconia membrane with its pore diameter of 0.07 μm as compared to the 0.16 μm pore diameter alumina membrane. This result could be expected because the relatively large oil droplets cause severe pore blockage of the 0.16 μm membrane in comparison with the smaller 0.07 μm membrane.

Major parameters that may influence filtration performance in the crossflow system are membrane pore diameter, transmembrane pressure, crossflow velocity, temperature, and backflushing efficiency. The crossflow velocity is one of the important parameters. Bhave and Fleming (9) reported that an increase in crossflow velocity from 0.8 to 4.1 m/s resulted in a permeate flux increase by a factor of about 2.4 under otherwise uniform conditions. This is a consequence of higher shear rates which

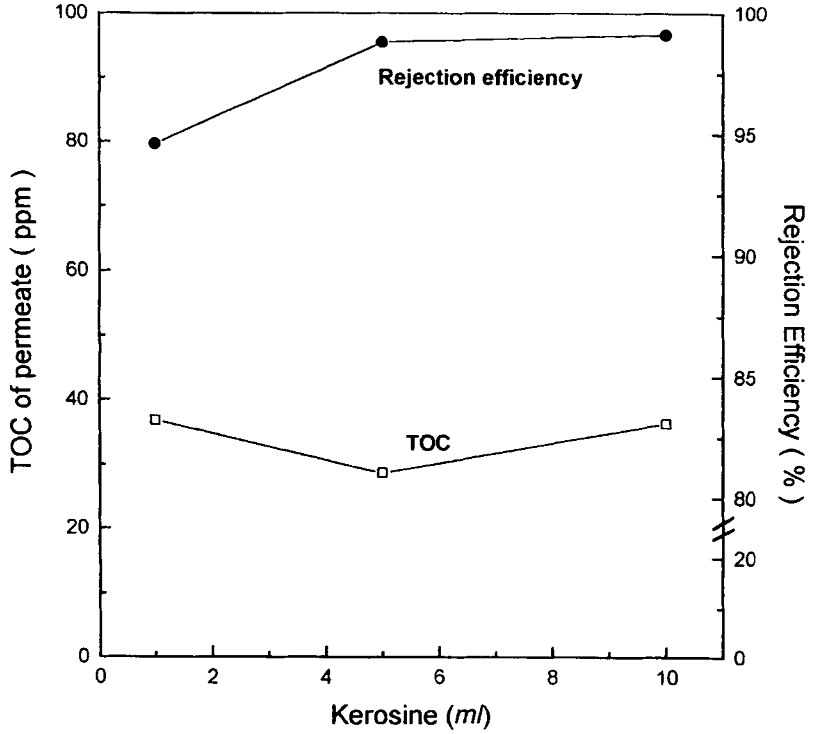

FIG. 10 TOC value of the permeate and rejection efficiency vs kerosene content in o/w emulsions containing 0.1 mL surfactant for the alumina membrane (transmembrane pressure 0.98 bar and crossflow velocity 0.27 m/s).

promote the efficient removal of accumulated particles rejected by the membrane and minimize blinding of the membrane surface. However, it is generally known that crossflow filtration is often helpful in slowing down membrane fouling but does not eliminate it. Backflushing can help remove excessive particle deposits on the membrane surface and also minimize the decrease in flux. The permeate flux in this work is somewhat low since the crossflow velocity is low at 0.27 m/s and backflushing was not applied. However, it is expected that the permeate flux would be increased satisfactorily by increasing the crossflow velocity and applying backflushing.

The oil rejection efficiency through the alumina composite membrane (Fig. 8) increased from 95.7 to 98% within a few minutes. It is believed that the oil rejection efficiency increased instantaneously in the early operating stage since the oil droplets, which are smaller than the average pore size of the alumina composite membrane, permeate through the membrane and fill the pore entrances of the membrane at the same time. On the other hand, the same phenomenon was lessened in the zirconia composite membrane due to its small pore size compared to the alumina composite membrane. The rejection efficiency through the zirconia composite membrane (Fig. 9) increased slightly from 96.7 to 98% after 40 minutes of operating time and then became constant. As shown in Figs. 8 and 9, the rejection efficiencies showed values below 100%. However, it is generally known that some of surfactant is dissolved in water rather than being adsorbed on oil droplets. During microfiltration, the soluble surfactant permeates through the membrane, and consequently increases the TOC value in the filtrate (i.e., low rejection efficiency). To evaluate whether the permeate contains kerosene or surfactant dissolved in water, oil–water separation was performed by varying the amount of kerosene and surfactant content in the oil/water emulsion. To minimize the effects of the oil layer deposited on the membrane, the transmembrane pressure were reduced to 0.98 bar at a constant crossflow velocity (0.27 m/s). Figure 10 shows the variation of oil–water separation efficiencies for the aluminia composite membrane with the amount of kerosene. The TOC value of the permeate was constant, while the separation efficiency showed a tendency to increase with an increasing amount of kerosene. This shows that the oil droplets could not permeate through the membrane. On the other hand, the TOC value of the permeate in Fig. 11 increased with the amount of surfactant. The separation efficiency remained constant in this case. This result indicates that the dissolved surfactant permeated through the membrane, in contrast to Fig. 10. From the above results it is concluded that oil–water separation efficiency was almost 100% when the effect of the dissolved surfactant is considered.

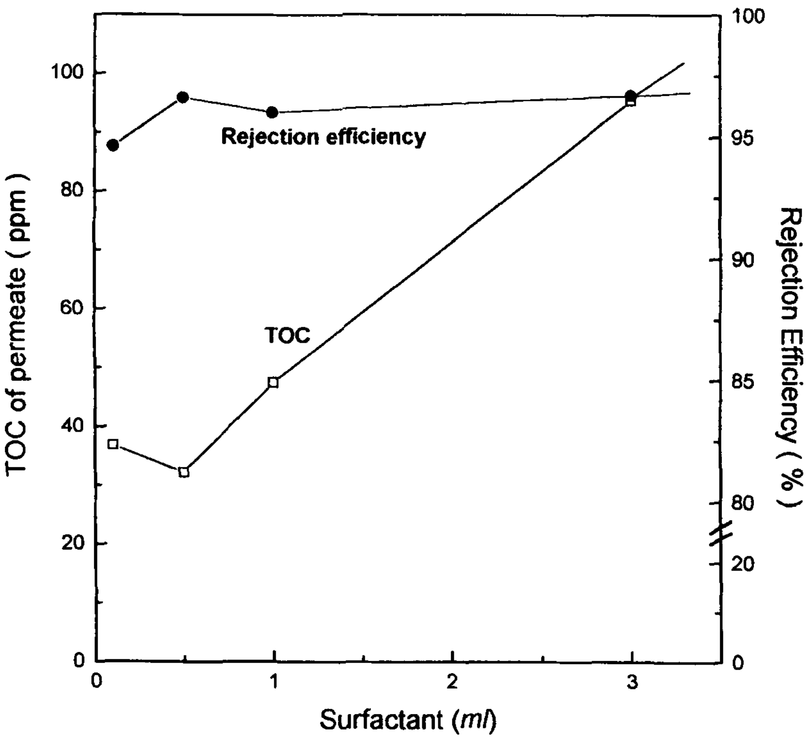

FIG. 11 TOC value of the permeate and rejection efficiency vs surfactant content in o/w emulsion containing 1 mL kerosene for the alumina membrane (transmembrane pressure 0.98 bar and crossflow velocity 0.27 m/s).

SUMMARY

Ceramic microfiltration membranes were synthesized by the reverse dip-drawing technique using an alumina/zirconia slurry, and then characterized by microstructural analysis and filtration performance for oil-in-water emulsion. The main results from this research are as follows.

1. Alumina and zirconia composite membranes without defects can be consistently produced by the reverse dip-drawing technique. The thickness of their top layers was appropriately controlled by the slurry concentration, while the minimum flow rate of the slurry for ensuring uniform thickness was about 40 mm/min.
2. The effective average pore sizes of alumina and zirconia top-layers are 0.16 μm and less than 0.07 μm, respectively. The existence of a

few large pores with a maximum pore size of 0.62–0.69 μm in the top layer did not reduce the oil/water separation efficiency.

3. The initial permeate fluxes of o/w emulsions through alumina and zirconia composite membranes were about 280 and 40 L/m²·h, respectively. Zirconia membranes showed less fouling than alumina membranes.
4. There was almost 100% removal of oil from o/w emulsions through the composite membranes synthesized in this study, as expected.

ACKNOWLEDGMENT

This work was financially supported by the Academic Research Foundation of Yonsei University in 1995.

REFERENCES

1. A. Zaidi, K. Simms, and S. Kok, "The Use of Micro/ultrafiltration for the Removal of Oil and Suspended Solids from Oilfield Brines," *Water Sci. Technol.*, *25*(10), 163–176 (1992).
2. P. Lipp, C. H. Lee, A. G. Fane, and C. J. D. Fell, "A Fundamental Study of the Ultrafiltration of Oil-Water Emulsions," *J. Membr. Sci.*, *36*, 161–177 (1988).
3. R. M. Dick, "Ultrafiltration for Oily Wastewater Treatment," *J. Am. Soc. Lubr. Eng.*, *38*(4), 219–222 (1982).
4. L. R. Harris, D. F. Jackson, and P. Schatzberg, "Oily Bilge Water Treatment with a Tubular Ultrafiltration System," *J. Eng. Ind.*, pp. 1215–1220 (November 1976).
5. G. Owen, M. Bandi, J. A. Howell, and S. J. Churchouse, "Economic Assessment of Membrane Processes for Water and Waste Water Treatment," *J. Membr. Sci.*, *102*, 77–91 (1995).
6. A. B. Koltuniewicz, R. W. Field, and T. C. Arnot, "Cross-flow and Dead-end Microfiltration of Oily-water Emulsion. Part I: Experimental Study and Analysis of Flux Decline," *Ibid.*, *102*, 193–207 (1995).
7. R. Villarroel López, S. Elmaleh, and N. Ghaffro, "Cross-flow Ultrafiltration of Hydrocarbon Emulsions," *Ibid.*, *102*, 55–64 (1995).
8. F. Falletti, "Method of Treating Polluted Oil-in-Water Emulsions or Microemulsions," US Patent 4,865,742 (September 12, 1989).
9. R. R. Bhave and H. L. Fleming, "Removal of Oily Contaminants in Wastewater with Microporous Alumina Membranes," *AIChE Symp. Ser.*, *84*(261), 19–27 (1988).
10. K. K. Chan and A. M. Brownstein, "Ceramic Membranes—Growth Prospects and Opportunities," *Am. Ceram. Soc. Bull.*, *70*(4), 703–707 (1991).
11. R. L. Goldsmith, "Special Issue on Ceramic Membranes," *J. Membr. Sci.*, *39*, 195–201 (1988).
12. K. Venkataraman, W. T. Choate, E. R. Torre, and R. D. Husung, "Characterization Studies of Ceramic Membranes. A Novel Technique Using a Coulter Porometer," *Ibid.*, *39*, 259–271 (1988).

Received by editor October 21, 1996
Revision received April 1997