Processing of Kaolin-Based Microfiltration Membranes

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1. Introduction

Compared to polymeric membranes, ceramic membranes have many potential advantages, such as excellent thermal, chemical and mechanical stability, longer life times, and simple cleaning processes.1-4 These properties make the ceramic membranes suitable for many applications, such as water purification, the removal of oil from oil-contaminated water, the clarification and sterilization of beverages, the concentrating of proteins in the food and dairy industries, and the recovery of lignin in the paper industries.5-10

Generally, the majority of ceramic membranes have been prepared from alumina (Al₂O₃), zirconia (ZrO₂), titania (TiO₂), and silica (SiO₂).11-15 and many research works have been carried out with those membranes or their composites. However, the application of ceramic membranes is considerably limited by the high cost of the above materials and related processing steps. Thus, many researchers have focused on the development of new types of cost-effective inorganic membranes, such as zeolite membranes16 and natural mineral-based ceramic membranes.17-22

Kaolin is often used as one of the raw materials in the synthesis of zeolite or mullite membranes.23-26 Zeolite hydroxysodalite was synthesized by a hydrothermal method using natural kaolin.27 Abbasi et al.28 processed mullite and mullite-alumina ceramic microfiltration membranes synthesized from kaolin and α-alumina for the treatment of oily wastewater. Chen et al.29 prepared macroporous mullite membrane supports through an in situ reaction sintering using kaolin combined with Al sources, Al(OH)₃, and AlF₃.

Kaolin can be a good material with which to fabricate low-cost ceramic membranes. Many researchers have reported the use of kaolin as a starting material with other additives for membrane applications.17-22 Bouzerara et al.26 fabricated ceramic membrane supports from kaolin-dolomite mixtures. The manufactured membrane supports are mainly composed of mullite, cordierite and anorthite phases, and their tensile strengths ranged from 6 to 15 MPa, which was likely acceptable as a support for microfiltration and ultrafiltration applications. Nandi et al.30 fabricated ceramic microfiltration membranes using kaolin, quartz, calcium carbonate, sodium carbonate, boric acid, and sodium metasilicate as raw materials, characterizing the feasibility of the membranes for juice processing applications. The results confirmed the greater applicability of low-cost ceramic membranes for beverage processing applications, in contrast to the widely applicable polymeric membranes. Vasanth et al.27 also processed low-cost ceramic membrane supports using kaolin, quartz, and calcium carbonate, sodium carbonate, boric acid, sodium metasilicate as raw materials by uniaxial dry compaction. The prepared supports offer good flexural strength (22 to 31 MPa) and chemical stability (< 2% weight loss in acidic media and no weight loss in basic media). Khe- makhem et al.31 prepared microfiltration membranes from Tunisian clay materials. The membranes consisted of a clay skin layer prepared by a slip-casting method deposited on a silty marls support. They demonstrated the possibility of...
the application of the membranes for cuttlefish effluent clarification. The above results\(^{17,22,29}\) suggest that low-cost ceramic membranes prepared from natural materials are likely readily applicable to areas such as beverage processing and wastewater treatment.

Studies using sodium borate (Na\(_2\)B\(_4\)O\(_7\)·10H\(_2\)O) as a bonding phase for kaolin have not yet been reported. Sodium borate melts at a temperature below 750°C. The low melting temperature suggests the possibility of the low-temperature processing of kaolin-based membranes. In the present work, ceramic membranes were fabricated by a simple uniaxial pressing route using kaolin and sodium borate as an additive. The effects of the additive content and the sintering temperature on the porosity and flexural strength of the kaolin-based ceramic membranes were investigated. In addition, the pore size distribution and permeability of a number of selected membranes were characterized.

### 2. Experimental Procedure

Commercially available kaolin (Al\(_2\)O\(_3\)·2SiO\(_2\)·2H\(_2\)O, extra pure, Samchun Pure Chemical Co. Ltd., Pyongtaek, Korea) and sodium borate (Na\(_2\)B\(_4\)O\(_7\)·10H\(_2\)O, first grade, Shinyo Pure Chemical Co. Ltd., Hyogo, Japan) powders were used as the starting materials. Sodium borate was added to increase the mechanical strength of the kaolin-based membranes.\(^{28}\) Five batches of powder mixtures were prepared with varying sodium borate contents: 0, 1, 2, 3, and 5 wt\% (see Table 1). All batches were mixed separately in a polypropylene jar for 3 h using distilled water and Al\(_2\)O\(_3\) grinding balls to make the raw materials homogeneous. Polyethylene glycol was added as a binder. The milled slurry was dried at 100°C for 24 h and was uniaxially pressed at a pressure of 50 MPa. The compacts were sintered at 900, 1000, 1100, and 1200°C for 2 h in air.

The bulk density of each ceramic membrane was calculated from its weight-to-volume ratio. The porosity was measured using the Archimedes method. The open porosity and pore size distribution of several selected samples were measured by means of mercury porosimetry (AutoPore IV 9500, Micromeritics, Norcross, GA, USA). The microstructures of the samples were observed by scanning electron microscopy (SEM, S4300, Hitachi Ltd., Hitachi, Japan). X-ray diffraction (XRD, D8 Discover, Bruker AXS GmbH, Germany) was conducted on the ground powders using CuK\(_α\) radiation. For flexural strength measurements, bar-shaped samples were cut to a size of 4 mm × 5 mm × 30 mm. Bending tests were performed at a crosshead speed of 0.5 mm/min using a three-point bending fixture with a span of 20 mm.

The permeability of several selected samples was measured by a capillary flow porometer (CFP-1100-AEX, PMI, New York, USA), and the gas permeability (\(\alpha\), specific permeability) was computed from the measured flow rate and pressure difference using Darcy’s law,

\[
\Delta p = \eta \frac{Q}{A} \frac{\alpha}{L}
\]

where \(\Delta p\) is the pressure drop from the entrance to the exit of the sample, \(L\) is the thickness of the sample, \(Q\) is the flow rate of air through the sample, \(\eta\) is the viscosity of air, \(A\) is the cross-sectional area of the sample, and \(\alpha\) is the permeability. Samples with dimensions of 3 × 30 × 25 mm were fixed in a sample holder with an O-ring and adhesive. Based on Eq. (1), the permeability was calculated from the slope of the line of the plot of \(\Delta p\) vs. \(Q\).

### 3. Results and Discussion

The XRD analysis of the samples showed that the starting clay powder was composed of kaolinite and sillimanite phases (Fig. 1 (a)). There was no phase change during sintering in the SB0 and SB5 samples, except for the SB5 sample, which was sintered at 1200°C (Fig. 1(b)). The XRD data of this sample (Fig. 1 (b)) clearly show the formation of \(\alpha\)-cristobalite. This indicates that the addition of sodium borate in an excess amount (5 wt% in this case) promotes the formation of \(\alpha\)-cristobalite, which may be derived from the partial decomposition of the sillimanite and/or kaolinite phases in the presence of molten sodium borate.

The effect of the sintering temperature on the microstructure of the clay-based membranes (SB3) is shown in Fig. 2. The microstructures consisted of large kaolin grains and a sodium borate bonding phase. The pressed compacts were heat-treated at 900-1200°C for 2 hr in air at a heating rate of 3°C/min. The heat treatment facilitated the melting of the sodium borate, and the molten sodium borate acted as a glue to bind the kaolin particles together. As shown in Fig. 2(d), kaolin particles were well bonded to each other by the molten sodium borate phase. The SB3 sample, sintered at 1200°C and with a porosity of 25%, consisted of strongly interconnected kaolin grains and large pores (Fig. 2(d)), whereas the SB3 sample, sintered at 900°C and with a porosity of 44%, consisted of loosely interconnected kaolin grains and small pores (Fig. 2(a)). The fracture mode changed from intergranular to transgranular with an increase in the sintering temperature from 900°C to 1200°C, indicating that the degree of bonding between the kaolin particles became stronger with an increase in the temperature. Sodium borate was transformed into a viscous liquid phase during sintering with little volume shrinkage and with the kaolin particles bound together.

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<th>Table 1. Batch Composition and Sample Designation</th>
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<td>Sample Designation</td>
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\(^1\)Samchun Pure Chemical Co. Ltd., Pyongtaek, Korea
\(^2\)Shinyo Pure Chemical Co. Ltd., Hyogo, Japan
Moreover, it was clearly visible that the pore size and pore structure changed with an increase in the sintering temperature. The structure of the kaolin-based membranes became dense and the pore size of the membranes increased with an increase in the sintering temperature. Fig. 3 shows the pore size distribution of the SB3 samples sintered at 1000°C, 1100°C, and 1200°C. This result shows a unimodal pore size distribution for all samples. The average pore diameter increased from 0.30 µm to 0.41 µm with an increase in the sintering temperature from 1000°C to 1200°C. This type of pore growth during an increase in the sintering temperature is frequently observed in many other porous ceramics. The pore growth was attributed to the pore coalescence occurring during the sintering process. The average pore sizes, ranging from 0.30 to 0.41 µm, correspond to the pore size of the ceramic membranes for microfiltration.

The effect of the sodium borate content on the microstruc-
The microstructure of clay-based membranes is shown in Fig. 4. The microstructure of the SB0 sample, sintered at 1100°C, consisted of loosely interconnected plate-shape kaolin grains, whereas the microstructure of the SB5 specimen consisted of well-interconnected plate-shaped kaolin grains. This was due to the difference in the fracture behavior. Mostly intergranular fracture was observed in the SB0 sample (no sodium borate added), whereas mostly transgranular fracture was observed in the SB5 sample (5 wt% sodium borate added). A greater amount of sodium borate added led to stronger bonding between the kaolin grains, resulting in a higher potential for the generation of transgranular fractures. The strong bonding between the kaolin grains was due to the formation of a vitreous mass by fused sodium borate and some of the impurities present in the kaolin. The starting kaolin powder contained impurities of 0.04% Cl, 0.05% Fe, 0.005% heavy metals, and 0.0002% As.

Fig. 5 shows the porosity of the kaolin-based membranes as a function of the sintering temperature. The porosity of the kaolin-based membranes ranged from 25% to 46% depending on both the sintering temperature and the sodium borate content. It was observed that the porosity decreased slightly from 900 to 1100°C later decreasing rapidly from 1100 to 1200°C. The dramatic decrease from 1100 to 1200°C was due to the enhanced densification of the kaolin-based membranes at 1200°C. The particles tend to agglomerate, leading to a more consolidated ceramic body at 1200°C. The porosity range obtained at different sintering temperatures decreased from 34-46% to 25-40% with an increase in the additive content from 1 to 5 wt%. A greater sodium borate addition promoted the densification of the membranes and decreased the porosity. The lowest porosity (25%) was obtained when the membrane containing 5 wt% sodium borate was sintered at 1200°C due to the partial filling of the pores by the viscous sodium borate flow and the resultant densification. A similar trend was also observed in sodium borate-bonded SiC ceramics.

The flexural strength of the kaolin-based membranes at different sintering temperatures is shown in Fig. 6. In general, the flexural strength trend was opposite to that of the porosity, ranging from 0.3 to 28.4 MPa. The strength generally increased with an increase in the sintering temperature and the additive content. The increase in strength was mainly due to the enhanced densification, i.e., decreased porosity. However, the flexural strength of the SB5 samples increased from 7.8 MPa to 19 MPa with an increase in the sintering temperature from 900°C to 1100°C, decreasing to 11.6 MPa when sintered at 1200°C. When we observed the surface of the SB5 sample sintered at 1200°C by means of SEM, many cracks on the surface were observed (see Fig. 7). These types of cracks were not observed in any of the other samples. XRD data of the sample (Fig. 1 (b)) clearly showed the formation of α-cristobalite. Thus, the cracks observed in the specimen were attributed to the phase transformation of the cristobalite as the sample cooled. Thus, an addition of sodium borate to kaolin exceeding the optimum content (most likely 3 wt% in the case) led to the formation of α-cristobalite, resulting in a decrease of the flexural strength. The
highest flexural strength (28.4 MPa) was obtained in the SB3 sample sintered at 1200°C. This strength is comparable to the strength values obtained in membranes prepared with Moroccan clay and kaolin-quartz mixtures.\textsuperscript{19,21} Flexural strengths of 10 MPa at a porosity level of 42% and 12 MPa at a porosity level of 35% have been reported in clay-based membranes.\textsuperscript{19} Ceramic membranes fabricated using kaolin, quartz, and calcium carbonate showed flexural strengths of 34 MPa at 30% porosity\textsuperscript{21} and 11 MPa at 39% porosity.\textsuperscript{36} Cordierite membranes showed flexural strengths of 7 MPa at 46% porosity and 30 MPa at a porosity level of 38%.\textsuperscript{32} The present results suggest that the addition of sodium borate will increase the strength of kaolin-based membranes when they are sintered at 900-1200°C in air.

Fig. 8 shows the specific air flow rate of the kaolin-based membranes sintered at 1100°C as a function of the pressure drop (\(\Delta p\)).

Fig. 8. Specific flow rate of kaolin-based membranes sintered at 1100°C as a function of the pressure drop (\(\Delta p\)).

Fig. 9. Air permeability of kaolin-based membranes fabricated at 1100°C for 2 h in air.

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with an increase in the additive content in the starting composition. The specific flow rate of the SB0 sample sintered at 1100°C(0.0025 L/min/cm\(^2\)) was 2.5 times higher than that of the SB5 sample sintered at 1100°C(0.0010 L/min/cm\(^2\)). The porosities of SB0 and SB5 samples were 43% and 37%, respectively. The permeabilities of the clay-based membranes are shown in Fig. 9. The permeabilities of the SB0, SB3, and SB5 samples sintered at 1100°C were \(2.64 \times 10^{-17}\) m\(^2\), \(1.85 \times 10^{-17}\) m\(^2\), and \(1.36 \times 10^{-17}\) m\(^2\), respectively. From Eq. (1), it is clear that the permeability is proportional to the flow rate. Specific permeability data based on Darcy’s law has not been reported yet for clay-based membranes. Permeabilities ranging from \(10^{-12}\) to \(10^{-13}\) m\(^2\) were reported in macro-porous SiC\textsuperscript{34} and mullite-bonded SiC ceramics with micron-size pores.\textsuperscript{35} Compared to the permeability of porous SiC, the permeabilities of the clay-based membranes are low. A further improvement in the permeability should be achieved by manipulating the porosity and pore size distribution. This can be realized by selecting the additive composition judiciously and by using clay powders with well-controlled particle size distributions.

4. Conclusions

Kaolin-based membranes with a pore size of 0.30-0.40 \(\mu\)m were successfully prepared by a simple pressing route using low-cost starting materials, kaolin and sodium borate. The present results suggest that ceramic membranes for microfiltration can be processed by a simple uniaxial pressing method with low-cost raw materials. The flexural strength increased with an increase in the sintering temperature and the additive content, whereas the porosity decreased as the sintering temperature and additive content increased. Both the air flow rate and the permeability decreased with an increase in the sodium borate content. The typical porosity, flexural strength and specific flow rate of a kaolin-based membrane sintered with 3 wt% sodium borate at 1200°C were 25%, 28 MPa, and \(2 \times 10^{-3}\) L/min/cm\(^2\) at a \(\Delta p\) of 30 psi, respectively.
Acknowledgment

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REFERENCES


