The preparation and characterizations of the diatomite-kaolin composite support layer for microfiltration

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Recently, porous ceramic membranes have become a subject of significant interest due to their outstanding thermal and chemical stability. To reduce the high manufacturing costs of these porous ceramic membranes, recent research has focused on the utilization of low-cost natural materials. Therefore, in this paper, we report the results of an attempt to prepare a diatomite-kaolin composite support layer that could effectively filter the ISO 12103-1 A3 test dust while exhibiting acceptable water permeability. The pore characteristics of the specimens were studied by scanning electron micrography, mercury porosimetry, capillary flow porosimetry, and a dead-end microfiltration system with particle counters.

Key-words : Diatomite-kaolin composite, Microstructure, Microfiltration

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1. Introduction

Porous ceramics have recently attracted great interest[1,2] for their unique properties such as low density,[2,3] low thermal conductivity,[3,4] and low dielectric constant.[5] Moreover, ceramic membranes[6-8] are among the most feasible applications of porous ceramics. Therefore, it is important to maintain precise control of the average pore size, largest pore size, mechanical strength, and permeability of the porous ceramic membranes while minimizing the material processing costs. Reducing the processing costs has limitations when simply altering the process conditions and utilizing commonly used, expensive high-purity ceramic materials, such as α-alumina, γ-alumina, zirconia, and silicon carbide. Therefore, in this study, we employed porous ceramic membranes prepared from diatomite as the matrix and kaolin as a strength enhancer, as both of these materials are inexpensive, natural, and abundant.

Diatomite is a sedimentary rock resulting from the siliceous fossilized skeletons of diatoms, which are composed of rigid cell walls called frustules.[9-12] Because the mechanical strength of a diatomite support layer is not an acceptable free-standing membrane, we introduced kaolin to tailor the pore characteristics of the diatomite support layer. Previously, we reported possible approaches for the fabrication of a diatomite-based support layer that allowed fine-tuning of the pore characteristics, such as the largest pore size and the mechanical strength, while retaining an acceptable level of air permeability. These approaches are as follows: (a) the air permeability of the diatomite support layer was enhanced beyond what was previously achieved by controlling the sintering temperature,[13-15] and (b) the largest pore size of the diatomite support layer was reduced through the formation of a diatomite-kaolin composite support layer,[16] through the formation of a diatomite-kaolin composite coating layer,[17] or through the deposition of an alumina coating layer.[18,19]

In previous reports, we measured only the air permeability of diatomite-based support layers to compare our results with the air permeability and/or water permeability of typical ceramic microfiltration membranes reported in the literature. However, at low flow rates, the air permeability of the specimens may be higher than the water permeability of the same specimens, because gas does not adhere to the pore walls the way liquid does and because the slippage of gases along the pore walls causes an apparent dependence of the permeability on the pressure (this is known as the Klinkenberg effect).[20] Therefore, in this study, we extended our investigation to include the water permeability of diatomite-kaolin composite support layers.

One of the major obstacles hindering more widespread applications of microfiltration is that water permeability declines over time. This phenomenon is commonly known as ‘membrane fouling’.[21] Membrane fouling significantly reduces the operation efficiency because the microfiltration system has to be stopped frequently to restore the water permeability through physical and/or chemical cleaning.[22] However, while membrane fouling of conventional ceramic membranes, such as α-alumina[23-27] and zirconia,[28-31] has been reported, there are only a few studies on membrane fouling of low-cost natural material-based ceramic membranes.[22,32,33]

Therefore, the present study investigates several important aspects. First, we determined whether the water permeability of the diatomite-kaolin composite support layer would decline sharply by pore blockage and cake formation due to the complexity of its pore structure or remain at a certain level. Secondly, we investigated whether the decline in water permeability of the diatomite-kaolin composite support layers resulting from the foulants could be recovered by back-washing without chemical cleaning.

2. Material and methods

Diatomite (Celite 499, Celite Korea Co. Ltd., Korea) was used for the preparation of the diatomite-kaolin composite support layer. The average particle size of the as-received diatomite and as-received kaolin were 12.79 and 1.53 μm, respectively. To enhance the sinterability of the diatomite particles, the average particle size of the diatomite was reduced by ball-milling.

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Distilled water was used as a solvent and the slurry was ball-milled for 24 h with an alumina ball-to-powder volume ratio of 2:1. To incorporate kaolin into the diatomite matrix, diatomite particles at quantities ranging from 0 to 100 wt.% (Kaolin, Sigma-Aldrich, USA) were mixed for 3 h by ball-milling with a ball-to-powder volume ratio of 0.5:1.

To extrude the diatomite-kaolin composite support layers, 15 wt.% of methyl cellulose (Methyl cellulose, Sigma-Aldrich, USA) as a binder, and 15 wt.% of distilled water as a solvent were added. The mixed slurry was aged for 48 h at room temperature, and extruded by a double screw extruder (KTE-50S, Kosentech, Korea). An extruded diatomite-kaolin composite support layer has flat tube-type dimensions (width 50 mm, height 4 mm, and length 200 mm), and it has 16 inner holes (width 2 mm and height 2 mm), as shown in Fig. 1(a). After extrusion, the specimens were dried for 24 h at room temperature. To burn-off the binder, the dried specimens were heat-treated at 400°C for 1 h and, finally, sintered at 900–1200°C for 1 h. The flexural strengths of the diatomite-kaolin composite specimens were measured by a four-point bending test (Instron 4206, Instron, USA). The pore characteristics of the diatomite-kaolin composite support layers were measured using a dead-end microfiltration system (MTS2000, Sam Bo Scientific, Korea) equipped with particle counters (PAMAS-4132, PAMAS, Germany). The particle separation characteristics were tested at room temperature via a rejection experiment using ISO 12103-1 A3 test dust (ISO 12103-1, A3 Medium Test Dust, Powder Technology Inc., USA) with average particle diameter of approximately 1.0 μm. The concentration of the ISO 12103-1 A3 test dust in-feed was a constant 0.02 g/L, and the operating transmembrane pressure was maintained at 1 bar. After the filtration of the ISO 12103-1 A3 solution for 0.5 h, the diatomite-kaolin composite support layer was backwashed with air at 3 bar for 10 s before being filtered again.

3. Results and discussion

Typical scanning electron microscope (SEM) images of the diatomite-kaolin composite support layer sintered at 1200°C for 1 h with the addition of 10 wt.% kaolin are shown in Figs. 1(b) and 1(c). With the addition of 10 wt.% kaolin, the microstructure of the diatomite-kaolin composite support layer exhibits only the typical microscopic features of the diatomite matrix. In addition, the needle-like interlocking structure of the mullite phase or the
plate-like girders of kaolinite inside the pore channels are not found in the diatomite-kaolin composite matrix. This may result from both the sintering temperature and the amount of kaolin not being high enough to induce a visible phase transformation of kaolinite.

Figure 1(d) depicts the X-ray diffraction (XRD) patterns of the diatomite-kaolin composite support layers with varying amounts of kaolin that were sintered at 1200°C for 1 h. When a diatomite-kaolin composite support layer with a low amount of kaolin was sintered at 1200°C for 1 h, the major phase present was cristobalite. In addition, the mullite phase began to appear as the amount of kaolin approached 25 wt.%. Consequently, we ruled any effects form a phase transformation of the plate-like kaolinite to the needle-like mullite phase on the pore characteristics of the diatomite-kaolin composite support layer with less kaolin added, such as 10 wt.% as already shown in Fig. 1(e).

The flexural strength of typical ceramic microfiltration membranes based on alumina[34] or silicon carbide[35] is often above 50 MPa, and the flexural strengths of clay materials such as mullite,[36] kaolin,[37] and diatomite[38] is usually below 30 MPa. In this study, however, a flexural strength of 19.67 MPa was measured for the diatomite support layer sintered at 1200°C for 1 h with no added kaolin, and a flexural strength of 29.04 MPa was measured for the diatomite-kaolin composite support layers sintered at 1200°C for 1 h with the addition of 10 wt.% kaolin. Considering the high air permeability, the low sintering temperature, and the low cost of the raw material, the flexural strength of a diatomite composite support layer is acceptable for microfiltration applications. The flexural strength of the diatomite-kaolin composite support layer can be enhanced further by increasing the amount of kaolin added, as we already reported.[16]

However, the air permeability of the diatomite-kaolin composite support layer decreased sharply, when more than 10 wt.% kaolin was added. Therefore, the amount of kaolin added to the diatomite support layer hereafter was set to 10 wt.%.

Figure 1(e) presents the air permeability and the largest pore size of the diatomite-kaolin composite support layers sintered at temperatures ranging from 900 to 1200°C. The results show that these properties increased near linearly with the sintering temperature. Taking into consideration the findings of the previous report[16] and those in the literature,[11,12] we found that sintered diatomite had similar microstructures up to 1200°C. In addition, when the sintering temperature was higher than 1200°C, we did not expect further enhancements of the air permeability or water permeability of the diatomite-kaolin composite support layer by increasing the average pore size. Therefore, the sintering temperature of the diatomite-kaolin composite support layer was set as 1200°C.

The pore size distribution of the diatomite-kaolin composite support layer with 10 wt.% kaolin and sintered at 1200°C for 1 h is shown in Fig. 2(a). The average pore size and the largest pore size of the diatomite-kaolin composite support layer were 1.09 and 0.99 μm, respectively. In this case, the largest pore size of the diatomite-kaolin composite support layer was less than the average pore size of the support layers that were observed in Figs. 1(e) and 2(a). This discrepancy usually occurs when the pore structure is complex and partly inter-connected, as is the case for the diatomite-kaolin composite support layer. The average pore size measured by mercury porosimetry, contained all of the open pores regardless of the pore type, including blind pores, cross-linked pores, and through pores;[20] whereas, in principle, the largest pore size measured by capillary flow porosimetry ensures that the pores are fully inter-connected and act as pore channels.

In general, if the particle size of the foulants is similar to the pore size of the membrane, blocked pores can occur. Meanwhile, when the particle size of the foulants is much larger than the pore size of a membrane, cake formation that is more easily removed may occur.[21,40] The particle size distribution of the ISO 12103-1 A3 test dust is shown in Fig. 2(b). The average particle size (number distribution) and the average particle size (volume distribution) of the ISO 12103-1 A3 test dust were 0.97 and 25.13 μm, respectively. Because the average particle size (number distribution) was approximately the same as the average pore size and the largest pore size of the diatomite-kaolin composite support layer, it was expected that the ISO 12103-1 A3 test dust would be a good foulant to determine the effects of foulants on the water permeability of the diatomite-kaolin composite support layer. Furthermore, because the average particle size (volume distribution) of the ISO 12103-1 A3 test dust was 25.13 μm, back-washing was performed to determine whether the decline in water permeability of the diatomite-kaolin composite support layers due to cake formation could be reversed without chemical cleaning.

Figures 3(a) and 3(b) shows the schematic diagram of the dead-end microfiltration system with particle counters and an image of the installed system in the laboratory, respectively.
Figure 4(a) shows the water permeability (pure water) of the diatomite-kaolin composite support layer measured by the microfiltration system described in Figs. 3(a) and 3(b). The water permeability curve starts with a rapid initial drop, followed by a gradual decrease, and ends at a steady-state condition. This trend correlates well with the water permeability curve of typical microfiltration membranes. The water permeability (pure water) of the diatomite-kaolin composite support layer was approximately $1.0 \times 10^3 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$. In the literature, the pure water flux of ceramic microfiltration membranes based on materials such as $\alpha$-alumina, $\gamma$-alumina, zirconia, or fly ash were $1.5 \times 10^3 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$, $1.6 \times 10^3 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$, or $2.0 \times 10^3$ to $5.0 \times 10^3 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$, respectively. Considering the high permeability compared to alumina support layers, the low sintering temperature, the acceptable mechanical strength, and the low cost of the raw material (unlike the costs of high-purity alumina or silicon carbide), the diatomite-kaolin composite support layer is a feasible candidate for microfiltration applications.

Microfiltration test results of the diatomite-kaolin composite support layers using the ISO 12103-1 A3 test dust are shown in Figs. 4(b) and 4(c). A decrease in the flux was observed in Fig. 4(b) due to reversible and irreversible fouling from direct filtration using the ISO 12103-1 A3 test dust. Figure 4(c) shows the rejection rate of A3 test dust is above 99.9% regardless of the particle size after the microfiltration test of the diatomite-kaolin composite support layer. It should be noted that the number of particles (y-axis) is in logarithmic-scale.

In general, the pores are more likely to be partially blocked, and the degree of pore blockage depends on the shape and the relative
Fig. 4(b). In practice, a dead-end microfiltration system is prone to re-clogging instantly by the ISO 12103-1 A3 test dust during the operation types, such as dead-end microfiltration and cross-flow microfiltration, and the effect of operation parameters, such as the applied pressure, the concentration of foulants, and the cleaning conditions on the water permeability of the diatomite-kaolin composite support layer remain important topics for future research.

4. Conclusion

In summary, the diatomite-kaolin composite support layer specimens were prepared with 10 wt.% kaolin, and sintered at 1200°C for 1 h. The water permeability (pure water) of the diatomite-kaolin composite support layer was maintained at $1.0 \times 10^{-7} \text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$ for 12 h as a steady-state flow. In dead-end microfiltration of the ISO 12103-1 A3 test dust, the water permeability of the diatomite-kaolin composite support layer was partially recovered by back-washing, and it was maintained at above $3.0 \times 10^{-7} \text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$ for 12 h without any chemical cleaning. After dead-end microfiltration, the rejection rate of the ISO 12103-1 A3 test dust is above 99.9% regardless of particle size.

In this study, as we focused on the feasibility of a diatomite-kaolin composite support layer as a microfiltration membrane; chemical cleaning on the surface of the diatomite-kaolin composite support layer was not employed. Therefore, the effect of the operation types, such as dead-end microfiltration and cross-flow microfiltration, and the effect of operation parameters, such as the applied pressure, the concentration of foulants, and the cleaning conditions on the water permeability of the diatomite-kaolin composite support layer are important topics for future research.

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