Fabrication and Characterization of Metakaolin Based Flat Sheet Membrane for Membrane Distillation

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Abstract. A low-cost flat sheet kaolin/metakaolin membrane was fabricated via a combined using phase inversion and sintering methods at different kaolin/metakaolin content and sintering temperature. The ceramic suspension with suitable viscosity was prepared by mixing the kaolin/metakaolin powder, Polyethersulfone(PESf) as a binder, N-methyl-2-pyrrolidone(NMP) as solvent and Polyvinylpyrrolidone(PVP) as a dispersant. The membrane precursor was then sintered in a controlled furnace to target temperature of 1200 °C,1300 °C, 1400 °C and 1500 °C. Then, the surface of the kaolin/metakaolin membrane was modified by 1H,1H,2H,2H-perfluorooctyltriethoxysilane (PFAS). Finally, the ceramic membrane was characterized using a scanning electron microscope (SEM) and a contact angle analyzer. It was found that by varying the kaolin/metakaolin contents and sintering temperatures; different surface morphologies of flat sheet membranes were obtained. Moreover, the successful grafting with PFAS was evidenced by the increase in contact angle from nearly equal to 3.7° to 142°. Thus, it can be generally concluded that the metakaolin based flat sheet membrane has desirable characteristics for membrane distillation applications in terms of hydrophobic effect and chemical stability ($<1\%$ weight loss).

Keywords: Metakaolin · Ceramic membrane · Phase inversion · Sintering · Membrane distillation · Grafting

1 Introduction

Many countries around the world, especially in most parts of Africa and Asia, suffer from a shortage of clean drinking water. In order to satisfy the need and ensure an adequate supply of clean water, membrane-based technologies for water purification are necessary. The effort made in the literature is dedicated to developing less energy-intensive

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and environmentally friendly water purification techniques. Membrane distillation is a membrane-based water purification technology in which the separation process takes place by a thermally driven distillation process combined with a microporous hydrophobic membrane separation process [1]. The driving force for membrane distillation is the vapor pressure gradient across the hydrophobic micro porous membrane due to the temperature difference between the feed, and permeate side of the hydrophobic micro porous membrane interface [1]. Membrane distillation appears to be a promising solution for the water purification and desalination whenever cheap, and abundant energy like low-grade waste heat or solar energy is available [2–5].

The most commonly used membrane materials for membrane distillation are porous hydrophobic membranes. These membranes can be fabricated from organic and inorganic materials. Organic membranes are made up of polymeric materials such as polypropylene (PP), polytetrafluoroethylene (PTFE), and polyvinylidene fluoride (PVDF). Polymeric membrane material commercially used for membrane distillation experiments in different membrane distillation configuration and membrane modules such as flat sheet, spiral wound, tubular, capillary, and hollow fiber [2, 6]. Inorganic membranes are made up of carbon, silica, zeolite, ceramic, various oxides (Alumina, Titania, Zirconia) and metals. Ceramic materials are the most commonly used materials for synthesis of inorganic membrane for the membrane distillation application. As compared to polymeric micro porous membranes, ceramic porous membranes can resist severe environments due to their high thermal stability, high chemical stability, excellent mechanical strength, biocompatibility, long lifetime, energy efficiency, availability and sustainability [7, 8]. These outstanding properties made inorganic micro porous membranes a primary candidate to be used for water purification and desalination applications. Many studies have been reported to explore ceramic micro porous membrane applications in membrane distillation [9–12]. In this study, kaolin was the primary raw material for ceramic membrane fabrication. It is locally available and from less expensive raw materials. An attempt has been made to fabricate kaolin based flat sheet membrane by combing phase inversion and sintering method. However, flat sheet ceramic membrane from kaolin was found to have very weak mechanical strength and difficult to handle during operation [10]. On the other hand, metakaolin based flat sheet ceramic membrane is expected to be hydrophilic due to the presence of hydroxyl groups (OH^-) on its surface. This hydrophilic property is not suitable for the membrane distillation process [13]. In order to improve the hydrophobic properties of ceramic membranes, it is necessary to modify the surface hydrophilic properties of metakaolin based ceramic membranes. According to Kayvani Fard et al. [14], there are three common methods in ceramic membrane hydrophobization, which are chemical modification, surface morphology modification and combination of chemical and morphology modifications [15]. Hydrophobic ceramic micro porous membranes are most commonly prepared by chemical surface modification. Among different modifying agents, grafting with perfluoroalkylsilanes (PFAS) is the most commonly applied, especially in membrane distillation applications [16–18].

Thus, the objective of the present study is to fabricate surface modified kaolin/metakaolin based flat sheet membrane by combining phase inversion and sintering techniques. The effect of kaolin/metakaolin loading and sintering temperature on the surface morphology of the kaolin/metakaolin based flat sheet membrane was investigated.

2 Materials and Methods

2.1 Raw Materials

A commercial kaolin powder (<1 μm, Sigma Aldrich., Belgium) was used as the precursor material and transformed kaolin to metakaolin by thermal treatment (calcination) in the range of 600–850 °C. Analytical grade Polyethersulfone (PESf, Radel 3100P, Solvay Advanced Polymer), Polyvinylpyrrolidone (PVP, VWR International, Belgium) and N-methyl-2-pyrrolidone (NMP, VWR International, Belgium) were purchased and used as a polymer binder, dispersant and solvent respectively. Deionized water was used as the non-solvent coagulation bath. 1H,1H,2H,2H-perfluorooctyltriethoxysilane (PFAS, 97%, VWR International, Belgium) was used as a grafting agent and ethanol ($>99.8\%$, Sigma Aldrich, Belgium), acetone and alkaline solution. The composition of the ceramic suspensions is listed in Table 1.

Table 1. Composition of the ceramic suspensions

Membranes	1	2	3	4
Kaolin/metakaolin (wt. %)	35	40	45	47
NMP (wt. %)	59	45	49	47
PES (wt. %)	5	5	5	5
PVP (wt. %)	1	1	1	1

2.2 Fabrication of Kaolin/Metakaolin Based Flat Sheet Ceramic Membrane

Kaolin/metakaolin powder (<1 μm) and PES was dried to ensure that no moisture was trapped in the particle. Then, the required quantity of NMP was taken in a 100 ml glass bottle and PES was slowly added over a period of one hour to form the polymer solution. After the polymer solution was formed, PVP was then slowly added as dispersed in a polymer solution. The mixture was stirred by hot plate magnetic stirrer for 2 h at 60 °C and after the polymer solution was formed, kaolin/metakaolin powder was then added into a polymer solution slowly and then milled in a planetary ball mill for 48 h to ensure that the kaolin/metakaolin powder and polymer solution were mixed well. The resulting suspension was degassed for 30 min at room temperature to eliminate the air bubbles. The viscosity of the casting suspension was measured instantly prior to the casting process using a rheometer at room temperature. After measuring the viscosity, the casting suspension was cast on a casting machine and left for the evaporation process to occur for 30 s prior to the solvent exchange in the coagulation bath. The cast slurry was left in the water bath for 24 h to let the phase inversion process to be completed. Afterward, the membrane precursors were dried at room temperature for 24 h. Before the sintering process, the membrane precursor was cut in (50 mm × 50 mm square shape). The membrane precursor was then suspended in the furnace and fired in a controlled furnace to 600 °C at a rate of 2 °C min–1 for 2 h, then to target sintering temperature (1200–1500 °C) with an increment of 100 °C at a rate of 5 °C min–1 for 4 h. Lastly, the furnace was cooled down at a rate of 5 °C min–1 to room temperature.

2.3 Preparation of Hydrophobic Kaolin/Metakaolin Based Flat Sheet Membrane

Four equal sizes metakaolin flat sheet membrane prepared at various sintering temperatures mentioned above were used for this treatment. Prior to the chemical modification, the sintered flat sheet membranes were cut in a square form and cleaned by ethanol, acetone and distilled water for 10 min respectively. The flat sheet membrane was dried in an oven at 105 °C for approximately 12 h. After that, all the membranes have been treated by using alkaline solution (NaOH at pH 10) for 8 h. The flat sheet membranes were completely immersed and soaked into a 2 wt. % FAS (1H,1H,2H,2H-perfluorooctyltriethoxysilane) in ethanol solution for 8 h to allow the coupling reaction to occur. After grafting, the modified membranes were then washed in ethanol, acetone and distilled water successively and dried at 105 °C for 12 h in an oven.

2.4 Characterization of Kaolin/Metakaolin Powders and Membranes

The particle size of kaolin/metakaolin was examined by particle size analyzer using a diffraction light scattering (DLS, Model CGS-3 Goniometer) machine. Thermogravimetric analyses (TGA, Model Q600, TA Instruments) were used to analyze the thermal behavior of kaolin/metakaolin. The method of Wavelength dispersive X-ray fluorescence (WD-XRF, Philips PW 2400) spectrometer elemental analyses of clays has been continually showing the class of alumino-silicates to which the analyzed material corresponds. The elements determined in clays have been presented as a relative percentage of the elements expressed as oxides in the whole sample. X-ray diffraction (XRD, Seifert 3003 T/T) using Cu-Ka 1 radiation at a scanning rate of 2°/min. The membrane thickness was measured using a digital micrometer. Furthermore, the structure of kaolin/metakaolin based ceramic membrane prepared with different kaolin/metakaolin contents and treated at a different sintering temperature was examined using a scanning electron microscope (SEM, Philips XL40 LAB6). The kaolin/metakaolin based ceramic membrane samples were cut into 20 mm × 20 mm size and placed in a metal holder, which was then sputtered by platinum under vacuum before testing. The images of kaolin/metakaolin based ceramic membrane were captured to examine the overall view and porous structure of kaolin/metakaolin based flat sheet membrane at different kaolin/metakaolin contents; 35 wt. %; 40 wt. %; 45 wt. %; and 47 wt. %. Contact angle measurement has been performed on membranes to evaluate its surface hydrophobicity before and after grafting. The contact angle measurement of the sample was performed by a sessile drop method using a contact angle analyzer (Kruss DSA 10Mk2) at room temperature. All contact angle readings were taken 15 min after 0.5 ml water droplet was placed on the membrane surface. Chemical stability tests of the grafted membranes with analytical grade hexane were properly carried out at room temperature.

3 Results and Discussion

3.1 Characterization of Starting Materials

The particle size distribution of the precursor material is a critical factor in the fabrication of the ceramic membrane. It has affected the movement of the particles in ceramic suspension during phase inversion. Particles smaller than 1 μm do show a remarkable movement due to its lightweight and produced the macroporous structure. On the other hand, particles larger than 1 μm particles tend to move downward due to gravity effect and produced a dense structure [10]. Different sizes of kaolin and metakaolin particles relatively affect the morphological characteristic of kaolin/metakaolin based ceramic membrane [19]. Table 2 shows the particle size distribution of kaolin and metakaolin powder used in this study.

Table 2. Particle size distribution of kaolin and metakaolin powder

Component	Diameter(μm)	Particle size distribution (%)
Kaolin	<1	100
Metakaolin	<1	100

Table 3. Chemical and mineralogical composition (XRF) of kaolin and metakaolin sample

Sample chemical composition (Weight %)								
Component	SiO_2	Al_2O_3	K_2O	Fe_2O_3	CaO	MgO	P_2O_5	Lol
Kaolin	50.1	34.90	4.5	0.84	–	0.24	0.11	9.00
Metakaolin	55.53	38.30	4.27	0.79	–	0.26	0.10	0.75

The XRD diffractograms result revealed that kaolin is more crystalline than metakaolin which supposed to be amorphous in nature. This result supports the XRF result presented in Table 3. The crystallinity of kaolin was demonstrated by the XRD analysis shown in Fig. 1. The metakaolin was produced by the thermal treatment of kaolin clay. After thermal treatment kaolin clay at temperature 700 °C and heating time 3 h, characteristic peaks for kaolin (2 Theta 12.52,20.5,25.02,35.08,38.5°) was disappeared and SEM images (Fig. 2a and b) which shows a flake-like structure of kaolin and platy structure of metakaolin [20].

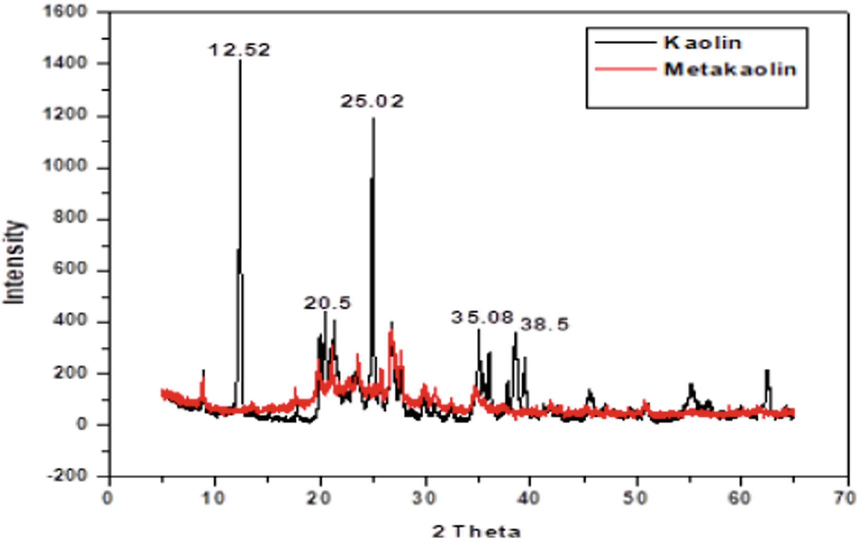
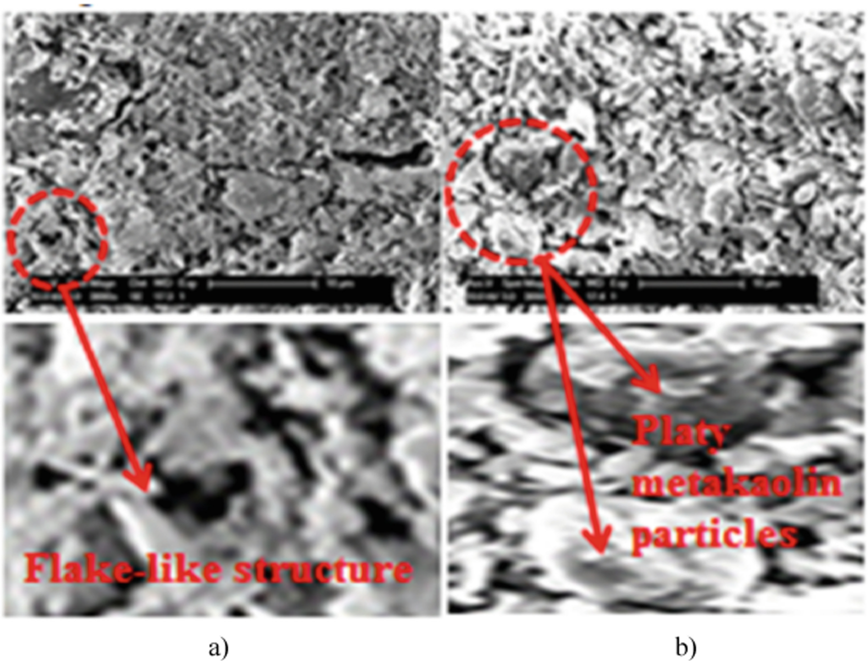


Fig. 1. XRD patterns of kaolin and metakaolin powder



a) b)

Fig. 2. (a) SEM images of the kaolin powder, (b) metakaolin powder

Figure 3 presents the TGA results of the kaolin and metakaolin. The TGA curve of kaolin shows a total weight loss of about 9%, which consists of two distinct regions. The first one between room temperature and 250 °C is due to the loss of physisorbed/bound water. The second one in the temperature range of 400 °C and 800 °C is mainly caused by the dehydroxylation of the kaolinite. In this region, phase transformation occurred (kaolin ($Al_2Si_2O_5$ (OH) $_4$) to metakaolin ($Al_2Si_2O_7$). The TGA curve of metakaolin shows no remarkable weight loss has occurred and stabilized at about 800 °C. Therefore, metakaolin is a preferred raw material for flat sheet ceramic membranes due to chemical composition and mineralogical qualities.

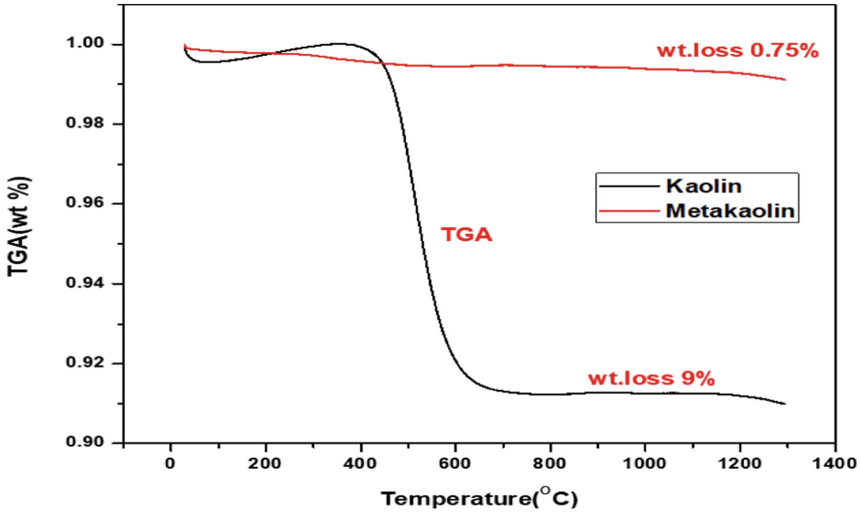


Fig. 3. Thermogravimetry analysis kaolin and metakaolin powder

3.2 Characterization of Kaolin/Metakaolin Flat Sheet Ceramic Membranes

3.2.1 Morphological Properties of Membranes

A significant shrinkage of the flat sheet precursor was observed during the phase inversion process. This is due to the rate of solvent (NMP) diffusion from the suspension is always faster than the rate of diffusion of water into the suspension. The dried flat sheet precursors were fired at various sintering temperatures mentioned above for sample kaolin and metakaolin in the controlled chamber (Nabertherm GmbH, Lilienthal, Germany). All the polymer binder components were expected to completely remove at 600 °C. The particle grain growth occurred at targeted sintering temperatures (1200 °C–1500 °C). Images of the precursor and membrane were recorded by using a digital camera. It can be clearly seen from the images (see Fig. 4), that the visualization of flat sheet membrane weight loss and shrinkage during sintering was higher as compared to the flat sheet precursor. A higher shrinkage of the flat sheet membrane was observed at elevated sintering temperatures. The increment in the shrinkage or densification of the flat sheet

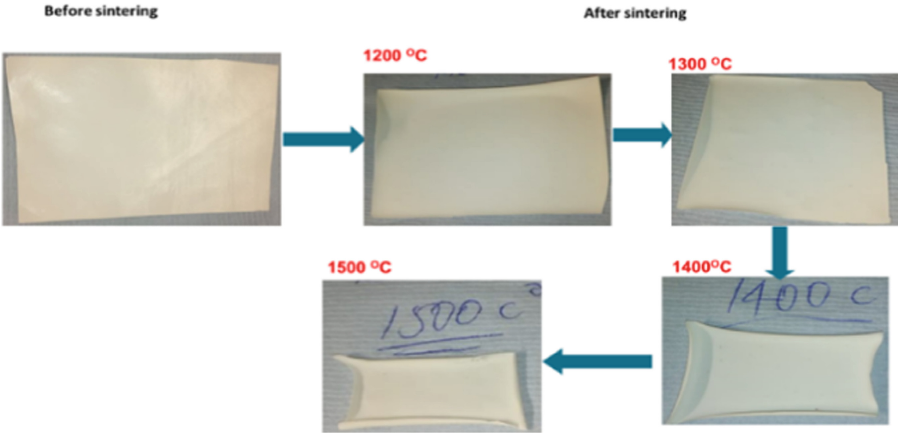


Fig. 4. Shrinkage of the flat sheet kaolin/metakaolin based ceramic membrane at a targeted sintering temperature (1200 °C–1500 °C).

membrane is due to the formation of sintering neck caused by the diffusion of the particles in the flat sheet membrane. Both types of membrane (kaolin and metakaolin based) got shrunk during phase inversion and sintering process. It is shown that the higher the shrinkage, the higher the internal stress generation. This results in more shape distortions and severe cracks or warps in the final sintered flat sheet membrane. It was found that the overall shrinkage of kaolin-based membrane was more than that of metakaolin based membrane due to completely removed organic substance from the ceramic precursor. The thickness of kaolin/metakaolin based membrane was measured and approximately 190 μm, indicating that the membrane is applicable for membrane distillation.

The prepared membranes were analyzed by SEM, and corresponding images are shown in Fig. 5. It can be concluded that the structure and surface morphology changed gradually with changing composition and sintering temperature.

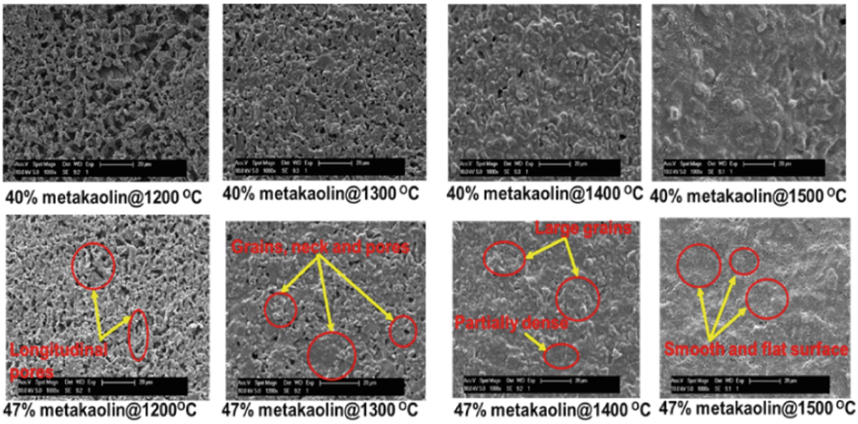
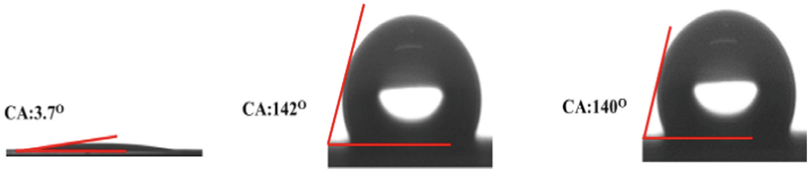


Fig. 5. SEM micrographs of the surface of the flat sheet metakaolin based ceramic membranes

Hydrophobic ceramic membranes are commonly prepared by chemical modification. The grafting process can be carried out by a reaction between OH-groups on the ceramic membrane surface and Si-O-alkyl groups of the silane [21]. As a matter of fact, the surface grafting process can be decreased the surface free energy and increased the contact angle of the membranes. During the sintering process at temperatures between 400 and 800 °C, the hydroxyl groups (OH^-) can be suppressed from the membrane surface. Therefore, alkaline pretreatment is required to restore hydroxyl groups (OH^-) on the membrane surface and allow more coupling reactions with PFAS. Water drops deposited on the flat sheet membrane forms a contact angle of 3.7° (super hydrophilic) (Fig. 6a). After surface modification, the contact angle becomes 142° (hydrophobic) (Fig. 6b), Confirming the transformation from hydrophilicity to the hydrophobicity of the membrane.

Fig. 6. The water contact angle of the membrane surface: (a) before grafting and (b) after grafting

Chemical stability tests of the grafted membranes with analytical grade hexane were properly carried out at room temperature. The test was repeated three times and the average value was reported. As the result is shown (Fig. 7) that, no membrane swelling, cracking, or breaking was observed. This is clear evidence that PFAS molecules were covalently bonded to the metakaolin based membrane and were stable in hexane.



under original conditions under grafted conditions after contact with hexane for 100 h

Fig. 7. Chemical stability tests of the grafted membranes (45% metakaolin @1200 °C)

4 Conclusion

The overall shrinkage of the kaolin-based membrane was more than that of the metakaolin based membrane due to the burning out of organic substance from the membrane. When the sintering temperature increased, the contact angle of the membrane increased, but the thickness of the membrane decreased. Based on the results discussed in the above sections, metakaolin based flat sheet membrane has desirable characteristics in terms of hydrophobic effect and chemical stability ($<1\%$ weight loss). Nevertheless, further research on the performance testing of the metakaolin based flat sheet membrane are required to effectively prepare the membrane for the intended applications.

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