

## Slip Casting of Alumina for Membrane Application

B. Darunee<sup>1\*</sup> & B. Tripob<sup>2</sup>

<sup>1</sup>Material Science Program, Membrane Science Technology Research Center, Faculty of Science,  
Prince of Songkla University (PSU), Songkhla 90112, Thailand

<sup>2</sup>Department of Physics, Prince of Songkla University 90112, Thailand

### ABSTRACT

Porous alumina membranes were prepared from alumina matrix, polyvinyl alcohol binder (1-5%) and calcium carbonate additive (0-3%). The disc-shaped alumina samples were fabricated by slip casting process. The alumina paste was sintered at different temperatures of 1100, 1200, 1300 and 1400°C. The results showed that the porosity of the porous membrane reached 45%-46% at 1300°C sintering for the mixtures of alumina matrix with 3% PVA and alumina matrix with 2% CaCO<sub>3</sub> plus 3% PVA. The water permeability was 150 L/m<sup>2</sup>.h at 20 kPa and the hydraulic conductivity coefficient was  $1.06 \times 10^{-9} - 2.43 \times 10^{-9} \text{ ms}^{-1} \text{ Pa}^{-1}$ . The density, linear shrinkage water absorption and mechanical strength were ca. 3.92 g/cm<sup>3</sup>, 1.61-1.71% and 20.45-21.92%, 17.26-21 MPa, respectively. The SEM micrographs of alumina membrane using PVA binder showed a dense surface layers. An increase of the PVA binder resulted in a higher pure water fluxes and bigger pore sizes. An increase of CaCO<sub>3</sub> in a 3% PVA binder mixtures resulted in a little decrease of porosity but increase in linear shrinkage from 1.57 to 2.04% at 1300°C sintering.

*Keywords:* Porous ceramics membrane, alumina, calcium carbonate, polyvinyl alcohol, slip casting

### 1.0 INTRODUCTION

The porous ceramics have been used for thermal insulation purpose as building materials for a long time. Nowadays, the use of ceramics membranes in separation processes has rapidly increased. Applications of porous ceramic as filters, catalyst supports and membranes are rapidly growing in the fields of environment, chemistry, biotechnology, foods processing and wastewater treatment. They can be used in harsh environments due to their high thermal and chemical stabilities and high mechanical strength. These porous ceramic membranes have attracted significant interest because of their potential uses in high temperature applications [1-4]. The properties (phase structure, mechanical strength, and the pore structure) of a thermally stable

membrane remain unchanged at high temperatures for a period of time [4].

For the uses in separation processes, the mesoporous ceramic membranes are deposited onto a macroporous ceramic support. Generally, ceramics membranes have a multi-layer structure including the substrate or support layer. The ceramics membrane supports can be prepared by several methods such as extrusion, slip casting, and isostatic pressing [5-8]. Slip casting is one of the most useful forming methods and is widely applied for the commercial production of ceramics because it is able to form compacts with large size and complex shape easily. In this process, the dispersion of ceramic powder in aqueous medium is required.

This work aimed at the preparation of ceramic membrane made of 99.4% alumina powder matrix, and studied the effects of calcium carbonate as a pore promoter or sintering aid and the effects of polyvinyl alcohol as a binder in the

\* Correspondence to: B. Darunee (email: darunee.b@psu.ac.th)

alumina matrix by slip casting method, at various sintering temperatures. Technological properties of the supports such as water permeability, porosity, pore size, morphology and structural strength were studied and reported.

## 2.0 EXPERIMENTAL PROCEDURE

The raw materials used were alumina 99.4%, calcium carbonate (Merck, Germany) additive and polyvinyl alcohol (PVA, Fluka 81383). Varying proportion of PVA binder of 1, 3 and 5% was chosen and coded 1 PVA, 3 PVA and 5 PVA, respectively. Similarly to the percentage of  $\text{CaCO}_3$  additive of 1, 2 and 3% was chosen and coded with the PVA proportions 1  $\text{CaCO}_3$ 3 PVA, 2  $\text{CaCO}_3$ 3 PVA, 3  $\text{CaCO}_3$ 3 PVA. The selected mixture formula was given in Table 1. Each mixture was wet grinding for 24 hour, aging for 1 day, control parameter in slip casting and viscosity 85-100 cp by Brookfield meter. At each mixture formula, totally 15 disc-shaped samples of 4.8 cm diameter and 0.3 cm thick were prepared by the slip casting method. The samples were then oven-dried at 110°C until constant weight, and sintering at temperatures 1100, 1200, 1300 and 1400°C for 1 h (heating at 4°C/min up to 600°C, and at 4°C/min from 600 to 1100-1400°C), and naturally cooled.

The linear shrinkage was determined according to the standard method ASTM C326 [9], upon firing, of the tested samples. Water absorption and related properties were determined following the

**Table 1** Six mixtures formula of alumina matrix, PVA binder (1-5 %) and calcium carbonate additive (0-3%) showing individual component weight percentage

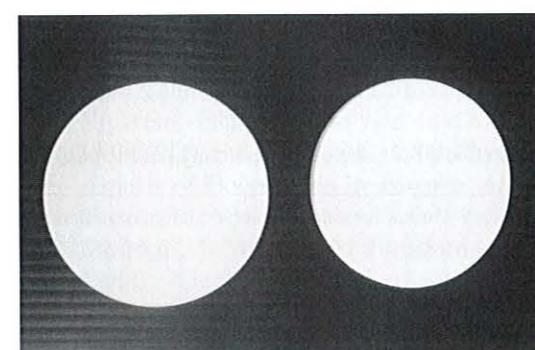
Mixture codes	Alumina (%)	PVA (%)	$\text{CaCO}_3$ (%)
1 PVA	99	1	-
3 PVA	97	3	-
5 PVA	95	5	-
1 $\text{CaCO}_3$ 3 PVA	96	3	1
2 $\text{CaCO}_3$ 3 PVA	95	3	2
3 $\text{CaCO}_3$ 3 PVA	94	3	3

standard method ASTM C373-88 (2006) [10]. For each mixture, the average property value was taken from five samples tested. The bulk density of the samples was measured by the water suspension method using Archimedes' principle. The morphology of phases and the microstructure were studied by the scanning electron microscope (SEM; JOEL Model JSM-58000LV, Japan).

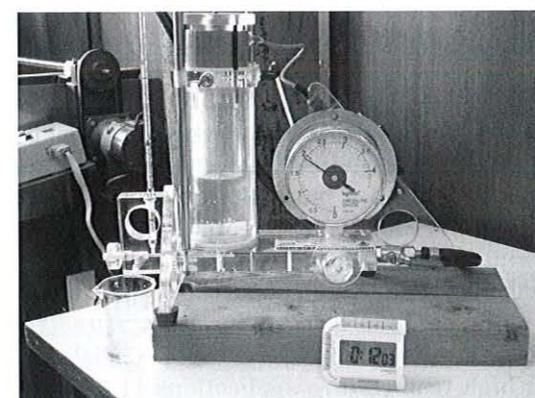
## 3.0 RESULTS AND DISCUSSIONS

### 3.1 Effect of Organic Additive (PVA) and $\text{CaCO}_3$

The shrinkage of sintered support was observed in Figure 1(a). The shrinkage of the sample



(a)



(b)

**Figure 1** Preparation of porous ceramic from alumina (a) disc-shaped samples and (b) dead-end cell for PWF test

sintered at 1400°C decreased from 4.3% to 3.9% as the PVA content increased (Figure 2(a)). Addition of  $\text{CaCO}_3$  content of 1, 2, 3% with fixed 3% PVA in alumina increased the shrinkage of the tested samples (Figure 2(b)) at the increasing sintering temperatures.

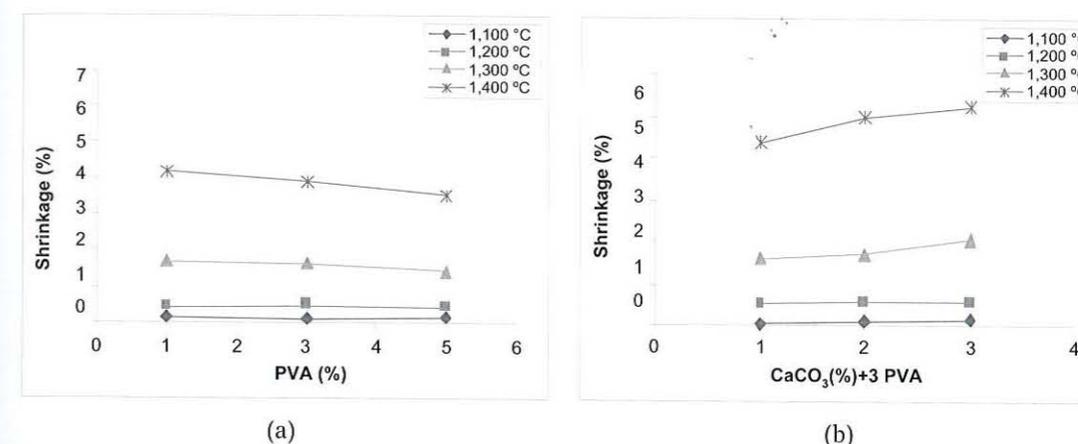
The porosity of the samples of 1-3-5% PVA sintered at temperatures 1100 and 1200°C ranged 45-52% but lower the porosity at higher sintering temperatures of 1300 and 1400°C (Figure 3(a)). Addition of  $\text{CaCO}_3$  of 1-3% behaved as a sintering aid clearly at higher sintering temperatures (Figure 3(b)).

The water absorption of the samples was generally decreased when the sintering temperatures

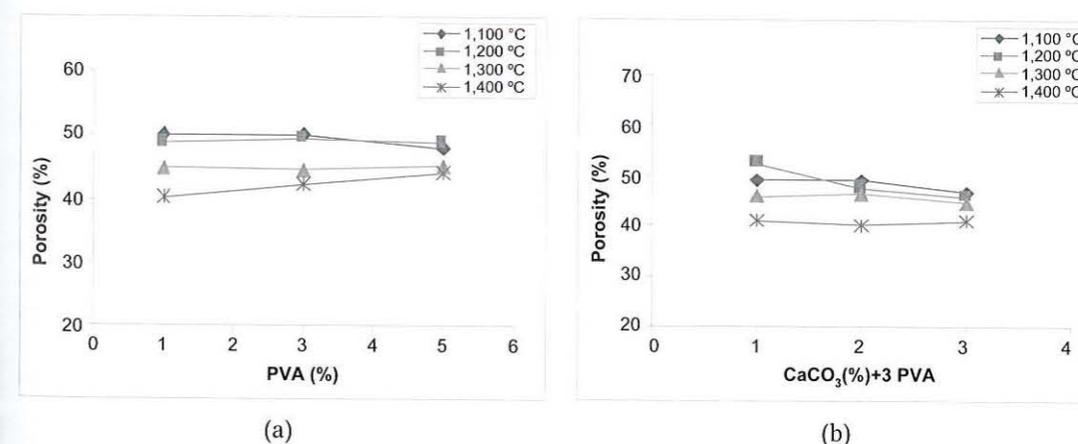
increased. For examples, the samples with 1% PVA, the water absorption was 26.00, 24.29, 20.69 and 17.14% for 1100, 1200, 1300 and 1400°C, respectively (Figure 4(a)).

### 3.2 Flexural Strength 3-point Bending Strength Test

Figure 5 shows the three-point bending strength of the samples sintered at different temperatures (1100-1400°C). The strength was enhanced with the increase of sintering temperature in the range of 1100-1400°C. When the temperature was above 1200°C, the strength of sample increased abruptly from 5 to 16 MPa. We concluded that



**Figure 2** Effect of shrinkage of the samples prepared at different sintering temperatures, from (a) the mixture coded 1-3-5 PVA, (b) the mixture coded 1-2-3  $\text{CaCO}_3$ 3 PVA



**Figure 3** Effect of porosity of the samples prepared at different sintering temperatures, (a) from the mixture coded 1-3-5 PVA, (b) from the mixture coded 1-2-3  $\text{CaCO}_3$ 3 PVA

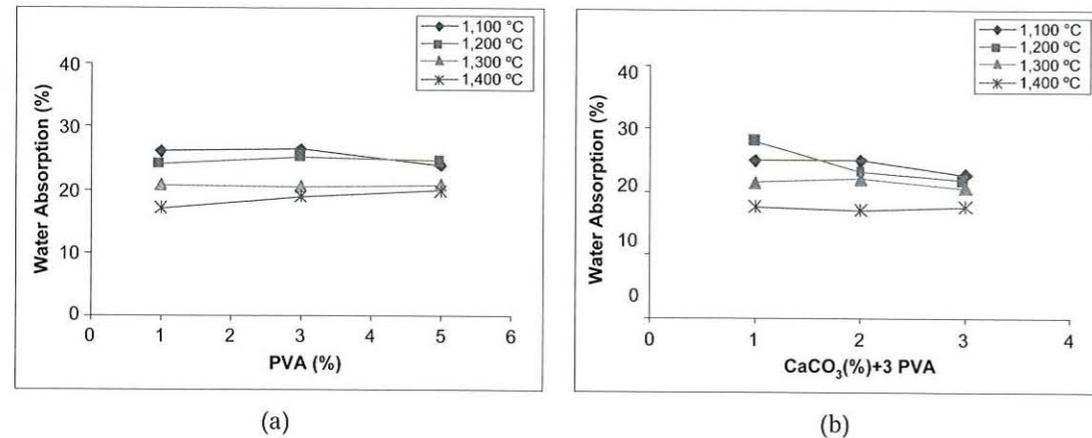


Figure 4 Effect of water absorption of the samples prepared at different sintering temperatures, (a) from the mixture coded 1-3-5 PVA, (b) from the mixture coded 1-2-3 CaCO<sub>3</sub>/3 PVA

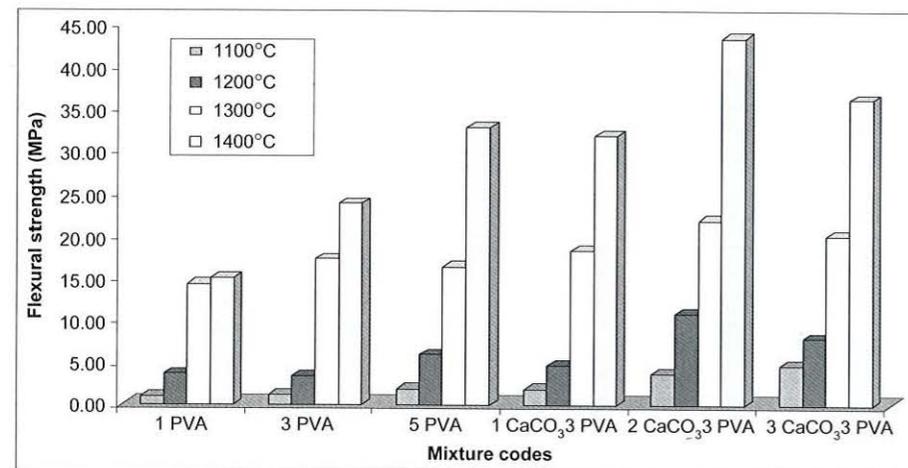


Figure 5 Strength of the samples prepared from the mixture coded 1, 3, 5 PVA and 1, 2, 3 CaCO<sub>3</sub>/3 PVA at different sintering temperatures

sintering temperatures of less than 1200°C could not produce a high strength porous alumina used for a support. The highest strength of 43 MPa was observed for samples coded 2 CaCO<sub>3</sub>/3 PVA at firing temperature of 1400°C. At this temperature, the porosity and water absorption were reduced to 39% and 16%, respectively, which were probably due to a high content of CaCO<sub>3</sub>. At such high temperature CaCO<sub>3</sub> probably behaved as a sintering aid instead of a pore promoter. This resulted in a lower in porosity and water absorption while the strength of the samples was increased. At a temperatures below

1300°C, CaCO<sub>3</sub> behaved as a pore promoter due to the transformation of CaCO<sub>3</sub> to CaO and CO<sub>2</sub> [11]. Addition of PVA in alumina increased the strength of the samples at the same temperature and increasing amount of CaCO<sub>3</sub> in the mixtures with 3 PVA resulted in farther increase of the strength, especially at 1400°C, while the porosity reduced.

We concluded that the best mixtures selected for preparation of porous alumina with the porosity of 45% and strength 18-21 MPa were the samples coded 3 PVA and 2 CaCO<sub>3</sub>/3 PVA, at 1300°C.

### 3.3 Pure Water Flux Test

The pure water flux (PWF) is measured under steady-state flow using the equation,  $J_w = Q/A\Delta T$  (1), Where,  $J_w$  is the water flux (L m<sup>-2</sup>h<sup>-1</sup>), Q is the quantity of water permeated (litre) during the

sampling time  $\Delta T$  (hour) and A is the membrane area (m<sup>2</sup>).

The hydraulic resistance of the membrane is determined by measuring the PWF at different transmembrane pressure ( $\Delta P$ ), ranged 20-100 psi (142-689 kPa). The membrane hydraulic resis-

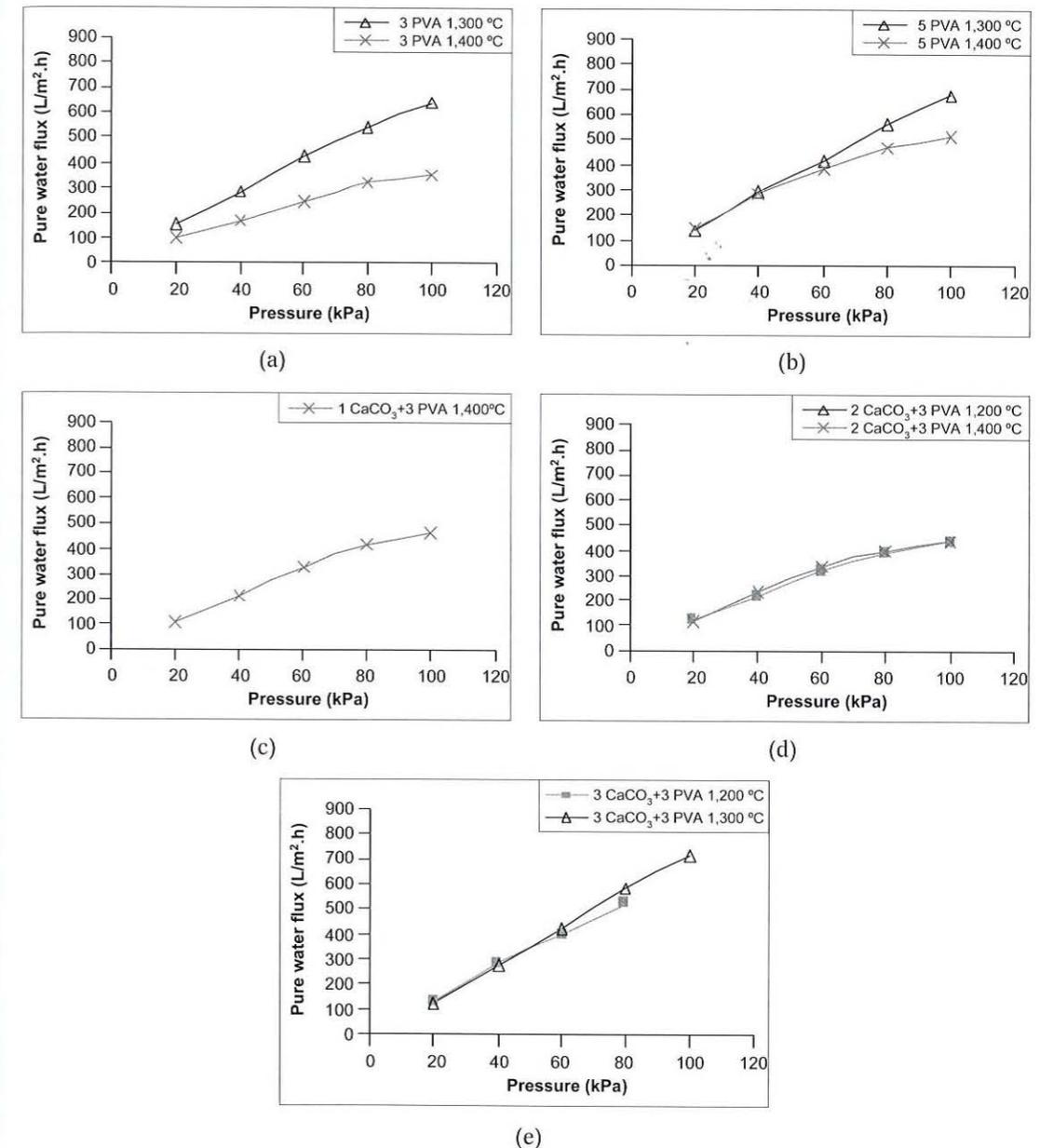


Figure 6 Pure water flux vs. pressure of the tested samples of the mixture coded (a) 3 PVA, (b) 5 PVA, (c) 1 CaCO<sub>3</sub>/3 PVA, (d) 2 CaCO<sub>3</sub>/3 PVA and (e) 3 CaCO<sub>3</sub>/3 PVA

tance ( $R_m$ ) is evaluated from the slope of the PWF versus transmembrane pressure difference ( $\Delta P$ ). Slope of the graph is the hydraulic conductivity coefficient ( $L_p$ ). The equations are the following,  $J_w = \Delta P/R_m$  (2) and  $J_w = L_p \Delta P$  (3), Where  $J_w$  is the water flux ( $l/m^2h$ ).

Figure 6 showed the effect of operating pressure on the pure water flux. Result indicated a linearly dependence of the pure water fluxes on pressures, especially at low pressures. At a high pressure some samples showed a little decrease of PWF which was observed as a non linear portion of the curves. The PWF becomes low in the case of low pressure at steady state flow. We investigated and found the transparent cake layer on the support surface even in the pure water flux studies. The cake layer on the support surface became a thin layer and gave a low permeation resistance at low pressure. On the other hand, at a high pressure the permeation fluxes were high and the cake layer on the support surface became thick and resulted in a lower the PWF because of a high permeation resistance [12]. Cake layer found on the support surface after some hours of the PWF tests was probably a bio-film which grew very quick in our humid environment.

Samples from mixture coded 3 PVA sintered at 1300°C had a higher PWF ( $280 L/m^2.h$ ) than those sintered at 1400°C ( $164 L/m^2.h$ ; Figure 6(a)) at the operating pressure 40 kPa. No PWF difference was observed when compared with those of samples coded 5 PVA (Figure 6(b)). Addition of  $CaCO_3$  1-3% did not increase the PWF of the tested samples (Figure 9(c), 9(d), 9(e)). The results indicated the highest PWFs were obtained from samples prepared from the mixture coded 3 PVA ( $641 L/m^2.h$ ) and 5 PVA ( $679 L/m^2.h$ ) with sintering temperature of 1300°C at 100 kPa. Table 2 showed the hydraulic

**Table 2** Hydraulic conductivity coefficient ( $L_p$ ) of the product ceramic membranes

Product Membrane code	$L_p$ ( $m.s^{-1}.Pa^{-1}$ )
3 PVA	$1.06 \times 10^{-9}$
5 PVA	$1.59 \times 10^{-9}$
1 $CaCO_3$ 3 PVA	$1.39 \times 10^{-9}$
2 $CaCO_3$ 3 PV	$1.35 \times 10^{-9}$

conductivity coefficients ( $L_p$ ) of the product membranes. The result indicated that the membranes coded 3 PVA, 5 PVA, 1  $CaCO_3$ 3 PVA, and 2  $CaCO_3$ 3 PVA can be used as a filtration membrane or as a porous support.

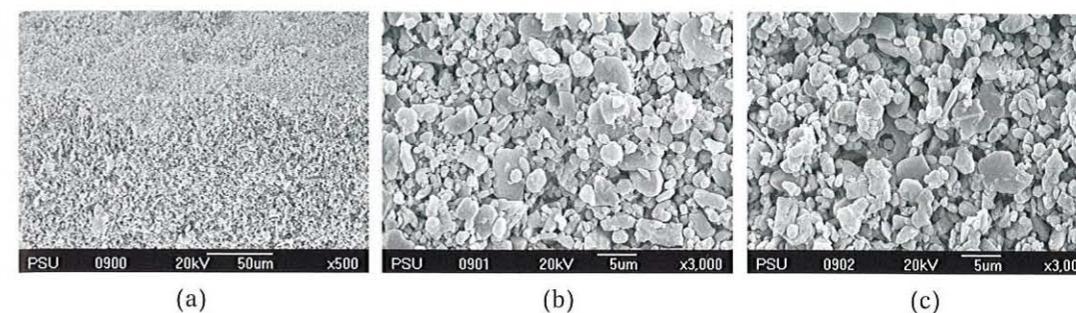
### 3.4 Morphological Studies

The cross-sectional, top surface and bottom support surface morphology of our alumina membrane were examined using a scanning electron microscope at different magnifications. Figures 7-10 showed the cross-sectional, top surface and bottom surface views of the produced ceramic membrane at different formula. It seemed clear that during the slip casting the fine particles combined with the PVA started to float to the top surface and produced the smaller pores at the top surface (Figures 7(b), 8(b), 9(b) and 10(b)) compared with the pores at the bottom surface (Figures 7(c), 8(c), 9(c) and 10(c)). Average pore sizes of membrane prepared from each formula estimated from SEM micrographs were present in Table 3.

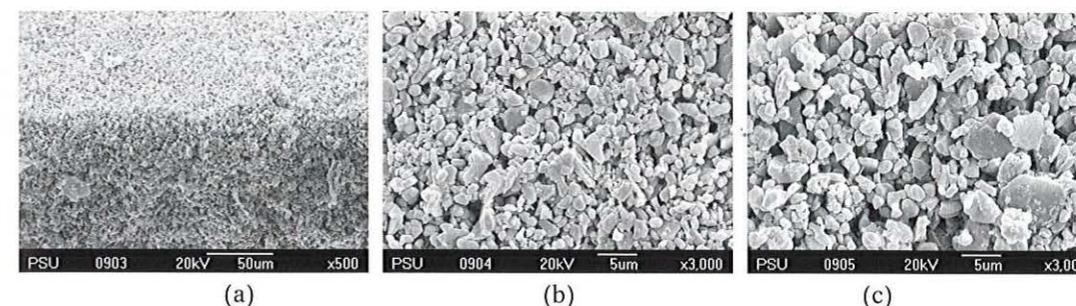
SEM images of sample formula coded 3 PVA showed the pore sizes ranged 0.8-1.5  $\mu m$  at the top surface (Figure 7(b)) and 1-2.5  $\mu m$  at the bottom support surface (Figure 7(c)). For formula coded 5 PVA, partial fusion was clearly seen and the pore sizes reduced to 0.15-2.0  $\mu m$  (Figure 8(b)) while the pore sizes at the bottom surface were similar to those at 3 PVA (Figure 8(c)). Addition of 1%  $CaCO_3$  in formula coded 1  $CaCO_3$ 3 PVA clearly showed a fusion enhancing effect of calcium carbonate and resulted in finer pore sizes (0.1 - 0.5  $\mu m$ ) and particle sizes at the top surface (Figure 9(b)). Similarly, the finest

**Table 3** Pore sizes at top and bottom surfaces of samples of different mixtures

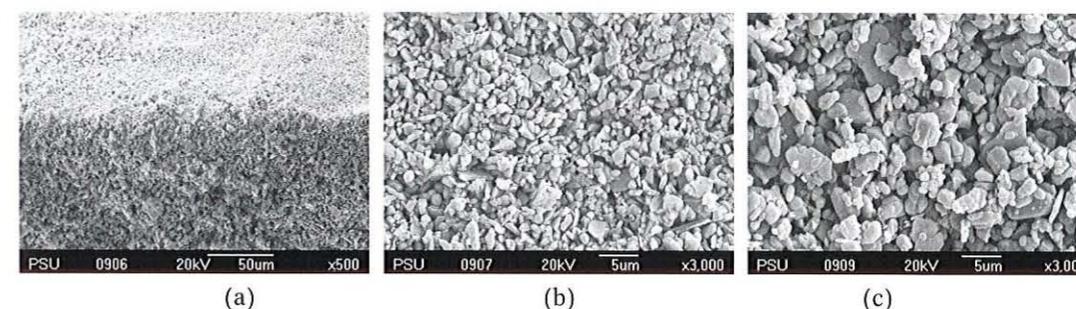
Mixture codes	Top surface pore ( $\mu m$ )	Bottom surface pore ( $\mu m$ )	Reference
3 PVA	0.8-1.5	1-2.5	Figure 6
5 PVA	0.15-2.0	1-2.5	Figure 7
1 $CaCO_3$ 3 PVA	0.1-0.5	0.1-1.5	Figure 8
3 $CaCO_3$ 3 PVA	0.05-0.3		Figure 9



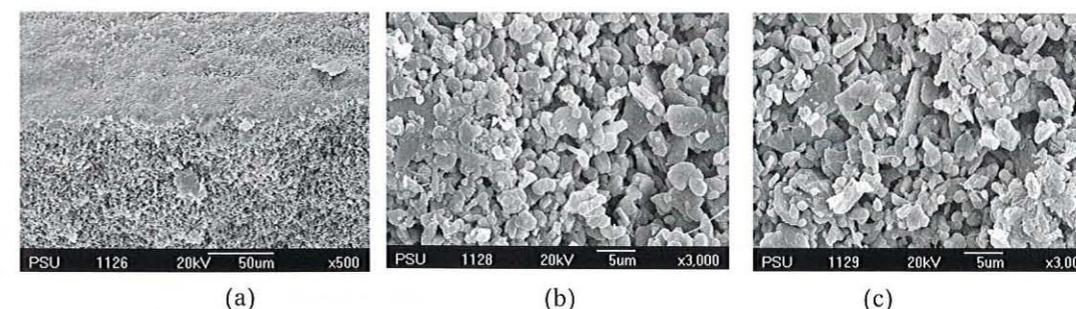
**Figure 7** The SEM images of the sample mixture formula coded 3 PVA sintered by 1200°C (a) cross-section (b) top surface and (c) bottom support surface views



**Figure 8** The SEM images of the sample mixture formula coded 5 PVA sintered by 1200°C (a) cross-section (b) top surface and (c) bottom support surface views



**Figure 9** The SEM images of the sample mixture coded 1  $CaCO_3$ 3 PVA sintered by 1200°C (a) cross-section (b) top surface and (c) bottom support surface views



**Figure 10** The SEM images of the sample mixture coded 3  $CaCO_3$ 3 PVA sintered by 1400°C (a) cross-section (b) top surface and (c) bottom support surface views

pore sizes (0.05-0.3  $\mu\text{m}$ ) at the top surface were resulted for the formula coded 3  $\text{CaCO}_3$  PVA sintered at temperature 1400°C (Figure 10(b)).

#### 4.0 CONCLUSIONS

The results showed that the highest porosity of the product porous membrane reached 45%-46% at 1300°C sintering for the alumina sample mixtures coded 3 PVA and 2  $\text{CaCO}_3$  PVA. The water permeability was 150  $\text{L}/\text{m}^2\cdot\text{h}$  at 20 kPa and the  $L_p$  was  $1.06 \times 10^{-9} - 2.43 \times 10^{-9} \text{ ms}^{-1}\text{Pa}^{-1}$ . The linear shrinkage and water absorption and mechanical strength were ca. 1.61-1.71%, 20.45-21.92% and 17.26-21 MPa, respectively. The SEM micrographs of alumina membrane using PVA binder showed a denser surface layer when compared with the bottom support surface. An increase of the PVA binder resulted in a higher pure water fluxes and bigger pore sizes. An increase of  $\text{CaCO}_3$  in a 3% PVA binder mixtures resulted in a little decrease of porosity but increase in linear shrinkage from 1.57 to 2.04% at 1300°C sintering.

Porous alumina support produced in this work has been further used in liquid effluent processing as well as in improving water drinking ability. Such supports will be tested in the removing polluting metallic species in wastewater produced by surface treatment in industry. Some kinds of composite membrane produced using alumina support will be tested for skim latex concentration.

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