Fabrication of Porous Ceramic Composite Clay-Zeolite Membranes via Replica Template Technique

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Abstract. Composite ceramic membranes are very popular due to their high-temperature resistance, reliable mechanical strength, resistance to acid/alkaline conditions, abrasive resistance, and long-term stability. As a filter, density and porosity are things that must be considered. Therefore, the construction strategy of composite ceramic membranes in controlling porosity is the main topic of this research. There are two advantages of adding zeolite to ceramic composite membrane materials. Besides being useful as a catalyst, Zeolite has the potential to increase porosity. The use of a Polyurethane (PU) sponge which has a greater density will have an impact on reducing the density of the composite. At the addition of 60% vol. PU 10 PPI and PU 12 PPI showed the lowest values, namely 2.48 g/cm^3 and 2.16 g/cm^3 respectively. In the CZ membrane material, the relationship between density and porosity is contradictory. If the density of the clay-zeolite composite ceramic membrane (CZ membrane) decreases, the porosity will increase. The highest porosity achieved in this study was 44.50% and 43.36% for PU 12 PPI and PU 10 PPI respectively. Observation of the micro and macro structures of the CZ membrane specimen with the addition of 3% vol. Polyvinylalcohol (PVA) shows an increase in the amount of porosity with increasing Zeolite content. However, it is different from the PU sponge which is used as a template replica media. The greater the PU sponge density, the lower the porosity, so the CZ membrane density value will increase. The detailed fabrication processes and mechanisms are reported in this review. The CZ Membrane is expected to be an alternative membrane material for the treatment of air, water, and other fluids. This is the result of membrane research which can be an important reference in the field of membranes made of ceramic composite materials.

Keywords: Porous Ceramic · Composite · Membrane · Replica Template · Zeolite

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1 Introduction

Porous ceramic composite materials are widely applied to biomedical and environmental materials [1], bone implants [2], catalyst carriers [3], membranes [4], water purification [5], gas burners [6], and thermal insulation materials in traditional buildings [7].

The processes for manufacturing porous ceramics composites can be divided into the following four categories, namely Partial sintering, Sacrificial fugitives, Replica templates, and Direct foaming [8]. The reason for choosing the replica template technique in this study is that the porosity and density obtained can be easily controlled. One way is to use the right PU sponge with the desired density. So that in the end a CZ membrane structure is obtained which is as expected. A replica template is impregnating a porous polymeric sponge or a natural porous structure with a ceramic (pre-ceramic) suspension [9].

Templates commonly used to build ceramic composite materials can be classified into two, namely organic templates and non-organic templates. In general, the non-organic template group is polymeric. The non-organic templates can be grouped into two, namely a polymeric sponge replica process and polymer foams as a template for catalyst supports [10]. Template polymers commonly used are polyurethane sponge [11] and polyurethane foam [12, 13]. Meanwhile, organic templates are natural templates such as wood, coral, sea sponges, etc. [14].

Clay is a mineral that is generally composed of several aggregates such as gibbsite, kaolinite, illite/mica, smectite, vermiculite, chlorite, iron oxide, quartz, non-crystalline, and others [15]. Since ancient times, clay has been popularly applied in the manufacture of ceramics using the sintering process [16]. Before sintering, the raw material is molded and dried in free air to form a ceramic green body [17]. The formation of the arrangement of the constituent particles greatly determines the physical and mechanical properties of ceramics. So it is necessary to strive for the arrangement of ceramic particles to be homogeneous. One way to overcome this is to make it into powder first with the powder metallurgy technique [18].

Clay has the potential to reduce the emission gas levels of motor vehicles properly. This aluminosilicate content causes the clay to have catalytic properties. In addition, clay is also composed of Fe_2O_3, MgO, and K_2O which are generally considered active promoters so that they can strengthen the catalytic power of clay. Another advantage of clay when applied in a high-temperature environment is in the case of energy-sensitive reactions due to the reformation of methane with CO_2, which is considered a constituent of biogas and major greenhouse gas [19, 20].

The combination of clay and zeolite can be used as a medium for treating liquid radioactive waste materials [21] as research conducted by Rosita (2016) that ceramic composites are made of 70% w/o clay-25% w/o zeolite-5% w/o charcoal has adsorption efficiency (60.36) and Decontamination Factor (2.52). While the concentration of Sr after filtration is still higher than the environmental standard for Sr-90, so this research needs to be continued to get optimal results.

(a) (b) (c) (d)

Fig. 1. Raw materials for research: (a) Clay, (b) Zeolite, (c) PVA, and (d) PU sponge

2 Materials and Methods

This section describes the materials and methods used in the research. Detailed explanations are described in each of the following subsections.

2.1 Materials

The research raw materials used in this study were Zeolite, Clay, PVA, and PU sponge as shown in Fig. 1. Natural zeolite was obtained from a local chemical shop in Semarang, Indonesia. Clay is obtained from the Kebumen region, Indonesia. PVA and PU sponges were purchased from a chemical store in Indrasari Semarang, Indonesia.

2.2 Methods

The method used in the manufacture of porous composite ceramics is by replicating a template using a PU sponge with a density of 10 and 12 PPI (pores per inch). Before being mixed, clay, zeolite, and PVA were crazed using ball milling. The raw materials used in making the specimens are powders that pass 100 mesh.

2.3 Samples Preparation

After being selected with 100 mesh, all the raw materials (clay, zeolite, and PVA) were mixed according to the ratio shown in Table 1. Then all the raw materials were mixed at 62 rpm for 15 min. To make it into a dough, water is added to the mixture as much as 15%vol. And blended at 62 rpm for 30 min.

Specimen printing was done with polyurethane sponge impregnation with dimensions of 15 mm × 15 mm × 15 mm. Impregnation was stopped after the pores of the PU sponge were filled with dough. Furthermore, the green body is allowed to stand for 24 h in the open air without being exposed to direct sunlight before sintering.

The sintering process was conditioned at 1000 °C for 60 min with a heating rate of 5 °C min by a furnace branded Neycraft JFF-2000. Specimen cooling is done by turning off the furnace OFF button. After reaching the ambient temperature, the specimen is removed from the furnace and ready for characterization testing.

Table 1. Composition of the materials used in this research

Sample	Clay (%vol..)	Zeolite (%vol.)	PVA (%vol.)	Abbreviation
1	60	40	3	C-40-Z
2	50	50	3	C-50-Z
3	40	60	3	C-60-Z

2.4 Characterization Methods

Bulk Density Measurement Approach in Porous Specimens
The density of sintered samples was determined according to the Archimedes method. The measurement begins with weighing the specimen in air and water. The measurement data is used to calculate according to the following formula: [22]

$$Density = \frac{Dry\ weight\ of\ sintered\ sample}{Weight\ loss\ in\ water} x\, 0.9965 g/cm^3 \tag{1}$$

2.5 Porosity Measurement

The pores formed in a material consisting of open pores and closed pores. But the actual volume does not include the pores. By knowing the bulk density and true density we can determine the porosity of the specimen based on the following formula: [23, 24].

$$Porosity = \frac{(D_{true} - D_{bulk})}{D_{bulk}} \tag{2}$$

$$D_{bulk} = \frac{M}{V_{bulk}} \tag{3}$$

$$D_{true} = \frac{M}{V_{true}} \tag{4}$$

where M is the mass, V is the volume and D is the Density of the specimen.

2.6 EDS Analysis

Before being used to make specimens, all raw materials are tested by EDS to determine their contents. Clay, zeolite, and PVA are displayed as elemental content in the percentage of elements of each raw material.

2.7 Macro Structure Analysis

Each sintered specimen was observed on the surface one by one using a microscope with a magnification of 100 X. The use of a low magnifying glass is expected to be able to see without blurring the connectivity between the pores in the specimen. Meanwhile, to find out the surface in detail, SEM is used.

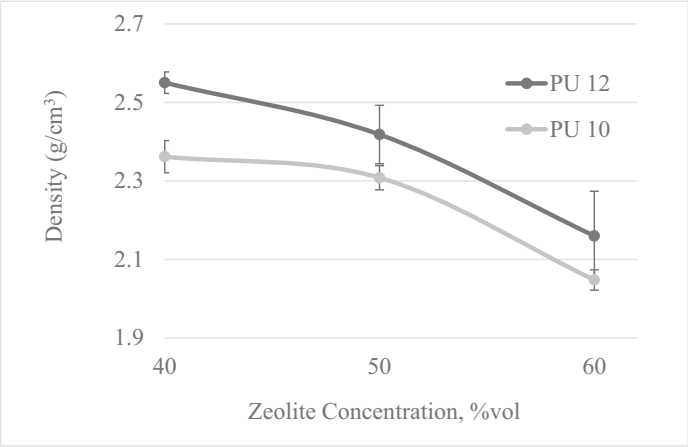


Fig. 2. Densitas dari CZ membrane

2.8 SEM Analysis

Surface morphology analysis of CZ membrane specimens using SEM (Scanning Electron Microscope). Before the observation, the test specimen was first coated with platinum for 55 s with a current of 30 mA. Then the specimens were analyzed using SEM at an accelerated voltage of 10 kV.

3 Results and Discussion

3.1 Density

The addition of zeolite content to the mixture can reduce the density of the CZ membrane material. The results of measuring the density of the CZ membrane material are shown in Fig. 2. Both using PU 10 PPI and PU 12 PPI, with increasing the Zeolite content, the density level of the CZ membrane will decrease. In the CZ membrane specimen with PU 10 PPI template, the lowest density was achieved by the specimen with the addition of 60% vol. Zeolite, which is equal to 2.48 g/cm^3. Whereas those using the PU 12 PPI template also showed the lowest value at the addition of 60% vol. Zeolite of 2.16 g/cm^3. The decrease in the percentage of CZ membrane density is due to the zeolite content which has a lower density than clay [22].

3.2 Porosity

Naturally, the relationship between density and porosity is mutually contradictory. If the density decreases, the porosity will increase, and vice versa. The results of the CZ membrane porosity test in Fig. 3 show results that are not contradictory. The addition of Zeolite can increase the porosity of the CZ membrane. This is justifiable and there is a correlation with the results of the CZ membrane density test (Fig. 2). The total porosity

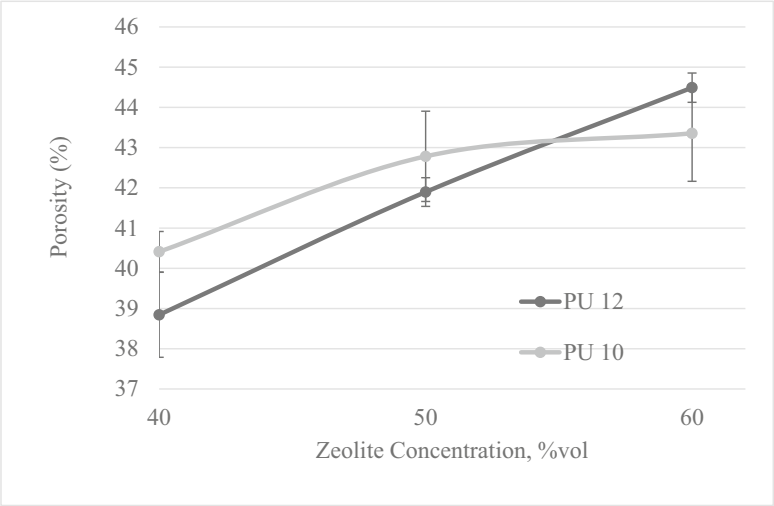


Fig. 3. Porositas dari CZ membrane

of the composite increases with a decreasing pore density of the PU sponge template [25].

Porosity measurements based on Archimedes' Law obtained the highest porosity achieved by CZ membrane specimens with the addition of 60% vo. Zeolite is equal to 44.50% and 43.36% for PU 12 PPI and PU 10 PPI respectively.

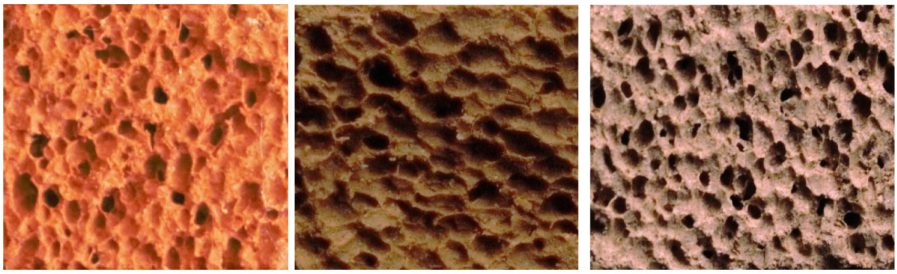
3.3 Morphology of CZ Membrane

The clarity of macro photos is affected by the magnification scale and the distance between the specimen and the microscope lens. Observation of the surface of the ZC membrane using a microscope at 50 x magnification shows the best image quality for observing the structure without interference. The surface of the CZ membrane shows a fairly clear porous cross-section. Even the difference in the variation of the cross-section of the macrostructure at various presented of volume. The zeolite is clear enough to be compared in Fig. 4.

The ZC membrane experienced an increase in the number of pores as the percentage of Zeolite increased. At the addition of 40% vol. Zeolite shows porosity that is still dominated by closed pores when compared to the other two specimens. While the addition of 50% vol. Zeolite shows between the two specimens. And at the addition of 60% vol. Zeolite shows the largest porosity size of all specimens. So, the results of this morphological observation have a supportive correlation with the results of the porosity test.

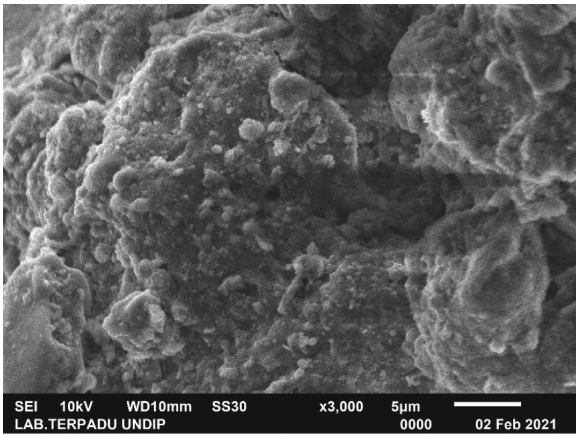
This is the case with observations made using SEM at a voltage of 10 kV. As shown in Fig. 4, the porosity formed by the PU sponge through the replica template method shows an irregular surface. The pore type formed is close porosity.

Observations with SEM as shown in Fig. 5 show a clear surface density of the CZ membrane. The CZ membrane using PU 10 as a template shows a rougher surface with

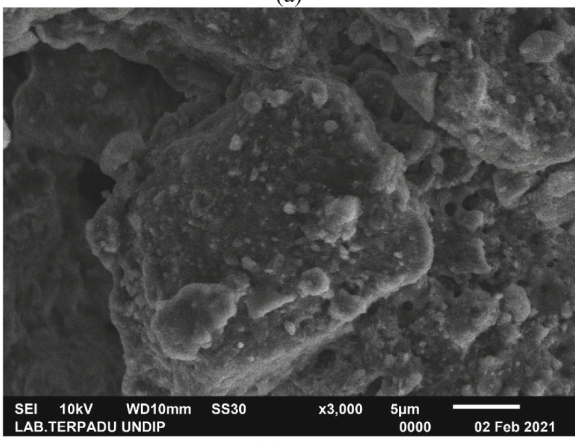


(a) (b) (c)

Fig. 4. The morphology of ceramic membrane: (a) 40% vol., (b) 50% vol. and (c) 60% vol.



(a)



(b)

Fig. 5. SEM morphology of CZ membrane: (a) PU 10 and (b) PU 12

a smaller pore size and a more dominant number. This shows that the number of porosity is higher and in sync with the results of the porosity test in Fig. 2.

The density level of the CZ membrane material using PU 12 shows superior results. This can be observed from its smoother surface and the marks left by the PU sponge.

4 Conclusions

CZ membrane manufacturing process with the addition of 3 vol. PVA with template replica technique was successfully carried out. The results of the CZ membrane specimen characterization test can be concluded that:

1. The use of a PU sponge which has a greater density will have an impact on reducing the density of the composite. At the addition of 60% vol. PU 10 PPI and PU 12 PPI showed the lowest values, namely 2.48 g/cm3 and 2.16 g/cm3 respectively.
2. In the CZ membrane material, the relationship between density and porosity is contradictory. If the density of the CZ membrane decreases, the porosity will increase. And vice versa, if the density increases, the porosity will decrease. The highest porosity achieved in this study was 44.50% and 43.36% for PU 12 PPI and PU 10 PPI respectively.
3. Observation of the micro and macro structures of the CZ membrane specimen with the addition of 3% vol. PVA shows an increase in the amount of porosity with increasing Zeolite content. However, it is different from the PU sponge which is used as a template replica media. The greater the PU sponge density, the lower the porosity, so the CZ membrane density value will increase.

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