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Use of Silica Gel from Volcanic Ash as Chitosan Composite Membrane's Filler

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This study aims to determine the process of making composite membranes of chitosan and silica fillers from volcanic ash of Sinabung mountain and determine the physical properties of chitosan composite membranes *viz.* degree of water absorption, functional groups. In this study, composite membranes were made using phase inversion method with the composition of chitosan and silica used were 2 g of chitosan and variations in dosage of fillers 0.6, 0.9 and 1.2 g of silica, while the stirring time was 8, 12 and 16 h. Based on the results , the best membrane conditions were obtained from composite membrane analysis with the best conditions of composite membranes at water absorption is 44.58 %. From the results of FTIR analysis, indicated the presence of OH bonds and Si-O-Si bonds on composite membranes caused by silica gel characteristics of composite membranes also supported by EDX analysis showed composite membrane contained carbon 55.17 %, oxygen 20.36 % and silicon 10.42 %.

Keywords: Chitosan, Composite, Membrane, Volcanic ash, Sinabung mountain.

INTRODUCTION

Composite membrane is a membrane consist of two layers with different polymeric materials which is the top layer supported by a buffer layer. The use of composite membranes is more beneficial because each layer has its own advantages which can increase selectivity, permeability and have high thermal stability [1,2]. In the manufacturing of membranes, it is necessary to add supporting material to obtain a membrane with good characteristics. One of the materials used for making membranes is chitosan and silica. Chitosan is a cationic polysaccharide which consists of glucosamine and *N*-acetylglucosamine residues which are bound by β(1,4)-glycosidic bond. Chitosan contains free amino groups that provide characteristics as a probe. However, limited solubility in chitosan causes limitations in its application. Many studies have been developed to overcome the problem of chitosan solubility in water, physical and chemical characteristics [3,4].

Silica gel is a granular like glass with porous form, silica is made synthetically from sodium silicate. Despite its name, solid silica gel, silica gel is a natural mineral that is purified and processed into one form of granules or beads. Silica is usually used for various purposes with a variety of sizes depending on applications needed such as in the tyre industries, rubber, glass, cement, concrete, ceramics, textiles, paper, cosmetics, electronics, paint, film, toothpaste, *etc.* . The advantages of silica gel are that they have high stability to mechanical influences, temperature, acidity conditions and high conductivity. These properties of silica gel make themselves to be used as an adsorbents, catalyst support materials, *etc.* [5,6]. The ionic conductivity of membrane added with silica is higher because silica can absorb water which functions as a proton transport medium in sulfonates so that ionic conductivity also increases and can increase membrane conductivity. In this study, volcanic ash can be used as silica, which can be applied in the manufacturing of composite membranes as fillers because it can increase the conductivity of composite membranes. Finally this membrane product can be applied in the filtration process and other benefits. Preparation of composite membranes in the previous study was carried out by combining chitosan with silica which obtained the best results in silica concentration of 5 % with a weight of 1 g chitosan. The results showed that the water swelling test and proton conductivity show increasing as nanosilica composition increases [7]. This is influenced by the hydrophilic group of Si-OH nanosilica, which can facilitate proton conduction.

EXPERIMENTAL

The material used chitosan was obtained from Faculty of Mathematics and Natural Sciences, silica was obtained from volcanic ash of Sinabung Mountain, NaOH, aquadest, acetic acid and hydrochloric acid were obtained from Rudang Jaya, Indonesia. The equipment used in this work were hot plate, 50 mesh sieve and 230 mesh sieve, filter paper, magnetic stirrer, funnel, measuring cup, oven and beaker glass.

Preparation of volcanic ash: The volcanic ash was sieved with a 230 mesh sieve to homogenize the ash size. The sifted ash was taken as much as 50 g and soaked with HCl and filtered. Then the ash washed and dried with oven.

Extraction of sodium silica solution: Volcanic ash was dissolved with 500 mL of 4 M NaOH and heated at 190 ºC with a variation of 120 min. Filtered and the filtrate was subjected for gravimetric analysis.

Process of making silica gel: The solution of sodium silica was dripped with HCl with a different concentrations to form a white gel with pH of 7. Silica gel was precipitated after 24 h and filtered, washed thoroughly with aquadest in order to remove the access acid and then finally dired in oven at 100 ºC.

Chitosan vomposite membranes containing silica fillers: Composite membrane synthesis was carried out using phase inversion method. First, 2 g of chitosan dissolved in 100 mL of 2 % acetic acid at room temperature for 2 h. Second, silica composition is 0.6, 0.9 and 1.2 g, respectively. then stirred at 600 °C for 8, 12 and 16 h. The homogeneous solution is also referred to as a dope solution which has no air bubbles, then the filtered solution is then poured onto a 20 cm × 20 cm glass mold and dried at room temperature resulting in a dry membrane. Dry membrane soaked with 1 M NaOH for 2 h then washed with aquadest to neutral pH and dried at room temperature.

RESULTS AND DISCUSSION

Energy dispersive X-ray spectroscopy (EDX): Fig. 1 showed the characteristic results of silica gel having composition O 39.74 %, Na 1.08 %, Al 6.21 % and Cl 1.01%. The results of EDX analysis also showed that the purity of silica gel was 51.96 % which is almost found similar as reported by Hendrasto *et al*. [8] that volcanic ash of Sinabung mountain contained 57. 01 % silica.

FTIR analysis: FTIR spectra of silica, chitosan and composite membrane are shown in Fig. 2. In the characteristics

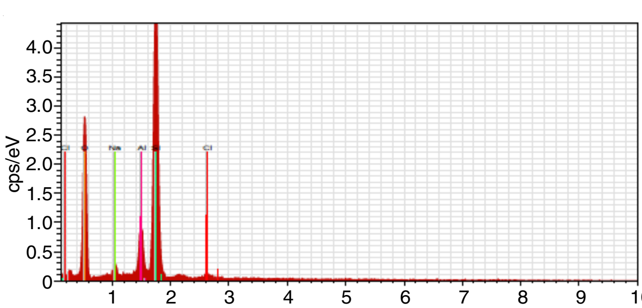

Fig. 1. Characteristic of silica gel using EDX

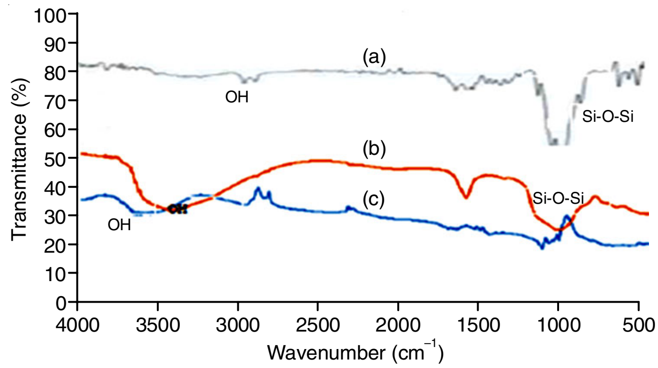

Fig. 2. FTIR spectra of chitosan composite membrane with silica gel filler from volcanic ash of Sinabung mountain (a), silica gel as fillers (b) and chitosan (c)

peaks of silica, the vibration peak of phenolic -OH is shown at 3437.15 cm^{-1}, etheral groups (-CO-) at 1064.71 cm^{-1}, Si-O-Si asymmetry stretching vibrations at 1200-400 cm^{-1}. Another peak at 470-430 cm^{-1} is due to the vibration of Si-O-Si buckling, while the peak at 1064.71 cm^{-1} showed a strong absorption uptake in the asymmetric stretch vibration of Si-O group in siloxane group (Si-O-Si). The vibration of buckling -OH groups of water molecules is shown at 1635.64 cm^{-1}. An alkane group (C-H) present in the chitosan is also visible at 894.97 and 999.13 cm^{-1}. The presence of absorption peaks at 1076.28 and 1149.57 cm^{-1} indicated the presence of alcohol groups, ethers, carboxylic acids and esters (C-O). The absorption peak at 1315.45 cm^{-1} indicated the presence of amine bond group (C-N). The absorption peak at 1651.07 cm^{-1} indicated the presence of anhydride bond group (C=O). Furthermore, there is an absorption peak at 2881.65 cm^{-1}, which indicates the presence of C-H alkane. The absorption peak at 3437.15 cm^{-1} is due to the presence of O-H groups [9]. In chitosan composite membrane silica gel fillers, Si-O-Si appeared at 1100-1000 cm^{-1}. The OH bond narrowed further with increasing silica contents and the more silica added, the higher the C-Cl and C-Br intensity. C-Cl is likely to exist from silica added because silica has undergone acidification using HCl, possibly HCl is still contained in silica [10].

Water absorption of composite membranes: The absorption value can determine the physical properties of membrane whether the membrane is waterproof or not. Water absorption also relates to the conductivity value of membrane. This is due to the role of water molecules in the conductivity of protons. Fig. 3 showed the effect of silica variation and stirring time on composite membrane water absorption. It can be seen that the water absorption capacity of the composite membrane has increased when the stirring time increased. Also, more amount of silica added, the absorbent degree also increased. If silica was dissolved in water for a long time, Si-OH will be formed. If the water absorption is more than 50 %, the membrane will be soft henceforth the membrane time will be shorter, so soft membrane cannot be used in the fuel cell because it does not function as a barrier between the two electrodes. Whereas if the water absorption of more than 50 % can be used for absorption and filtration [11].

Based on the absorption results (Fig. 3), composite membranes are suitable to use in the fuel cell membrane were stirred

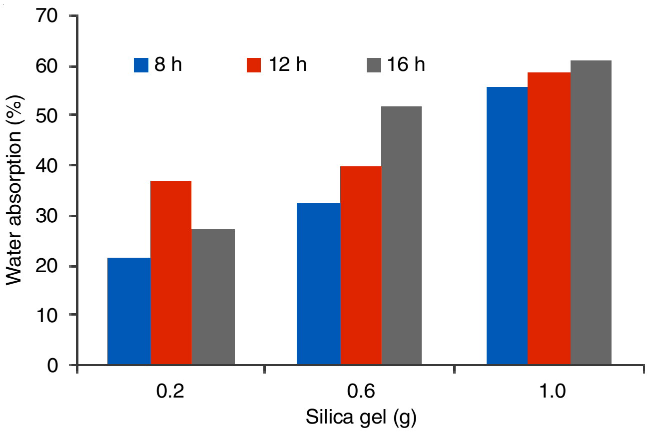

Fig. 3. Relation between time of stirring and addition of silica to composite membrane water absorption

at the addition of 0.6 g of silica at stirring time were 8, 12 and 16 h. The degree of water absorption was found to be 21.43, 36.90 and 27 22 %. When added 0.9 g at different stirred 8, 12 and 16 h the degree of water absorption was 32.77, 44.58 and 51.74 %, respectively. Whereas in the composite memb-rane with the addition of 1.2 g of silica and stirring time of 8, 12 and 16 h the degree of water absorption was 55.71, 58.89 and 61.27 %, respectively. The most optimum composite memb-rane is achieved when added silica is 0.9 g at 12 h of stirring time. Overall, the results showed that the greater the filler of membrane and the stirring time resulted in a higher degree of water absorption. Previous work on composite membranes from chitosan showed similar results where the degree of absorption obtained was greater with the addition of silica [12].

Energy dispersive X-ray spectroscopy (EDX) analysis of chitosan composite membrane: EDX analysis was carried out to determine the composition of the elements contained in chitosan composite membrane. The analysis was carried out on a chitosan membrane filled with silica 1.2 g silica with a stirring time of 16 h, because chitosan composite membrane with silica filler 1.2 g of silica has a high flux value.

Based on the elemental composition of EDX analysis in Fig. 4 can be seen that the composite membrane with the

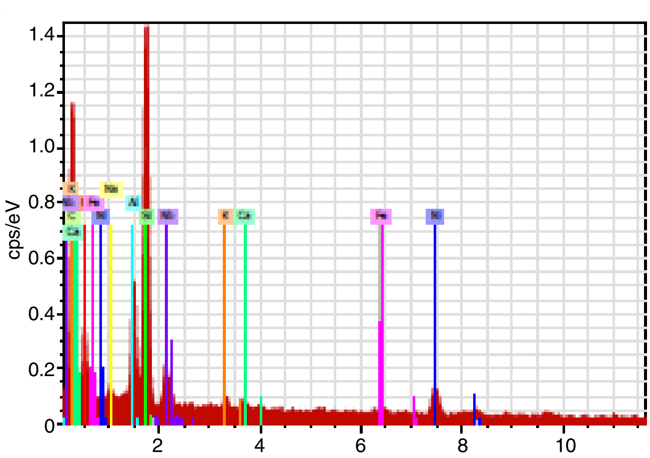

Fig. 4. EDX analysis of composite membrane containing 1.2 g of silica with stirring time of 16 h

addition of 1.2 g of silica with a stirring time of 16 h consist of carbon 55.17 % by weight and 70.11 atomic percent; oxygen 20.36 % by weight and 19.42 atomic percent while silicon is 10.42 % and the atomic percent is 5.67. These elements come from the main and supporting ingredients in the manufacturing of membranes.

Conclusion

In this work, the volcanic ash of Sinabung mountain of Indonesia is used for the preparation of silica and utilized as fillers in chitosan composite membrane is described. It is found that the greater amount of membrane filler and more stirring time resulted in the higher degree of water absorption. The FTIR analysis showed the presence of silica compounds in the composite membrane, water absorption capacity is 44.58 % and EDX analysis showed composite membranes with the addition of 1.2 g silica contains carbon 55.17 %, oxygen 20.36 and silicon 10.42 %.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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