Synthesis and characterization of clay filled polysulfone membran: the effect of composition and calcination of clay

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Abstract

A clay mineral is a potential candidate for the filler of molecular composite since it is a compound of layer silicate. The factors that would have to be considered in choosing clay as filler were cost, availability, physical properties, thermal stability, and chemical resistance. In this paper we attempted to synthesize membrane from polysulfone (PSF), polyethyleneglicol (PEG), N.N-dimethyl acetamide (DMAc) and clay, as main polymer, additive, solvent, and filler respectively. Clay used were from South Lampung, Indonesia, which were identified by XRD; consist of montmorillonite, chabazite, and cliptonilolite. Compositions of dope solution were 4.5 g PS, 4.5 g PEG, 14 g DMAc, while that of clay were 3, 4, 5, and 6 w % PSF. Calcinations temperature were 300, 350, 400 and 450 ^{0}C. Membrane was found to be in micro filtration, range with percent rejection of dextran T 500 were 30-48% with permeation of 45.76- 642.18 $Lm^{-2}h^{-1}atm^{-1}$ for pure water flux and 12.80-501.71 $Lm^{-2}h^{-1}atm^{-1}$ for dextran T 500, respectively. Composition of Clay 4 wt.% PSF without calcination gave the best properties of membrane.

Keywords: Polysulfone, Clay, Calcination, micro filtration.

1. Introduction.

Many new types organic/inorganic hybrid materials have the potential to combine the desired properties of inorganic and organic systems, improving the mechanical and thermal properties of inorganic ones with the flexibility and ductility of organic polymers. Organic-inorganic polymer hybrids constitute now an emerging research, which has opened the possibility of tailoring new materials, combining properties of inorganic glasses and organic polymers. Organic polymers are less chemical and temperature resistance. The others side properties of inorganic membrane materials render them more chemically, structurally, and thermally stable when compared to organic membrane, but inorganic membranes still have technical limitations and suffer from problems such as brittleness and lack of surface integrity.

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Polymer hybrids have a great potential for the design of innovative membranes, which has been relatively seldom explored up to now. For membrane application the use of hybrids is an open and promising strategy, which may combine characteristics both of inorganic and organic polymeric membrane and may contribute to solve some problems connected to each one of them.

An incorporation of inorganic network such as silica phase into an organic polymer matrix has been extensively studied because it displays wide range multifunctional properties [1–5]. A clay mineral is a potential candidate for inorganic filler of molecular composite since it is a compound of layer silicate. The factors that would have to considered in choose of clays, as filler were cost, availability, physical properties, thermal stability, and chemical resistance. Polymer-clay nanocomposite have emerged as new class of materials in the last decade of the 20th century. They have superior properties such as higher tensile strength, heat resistance compare with traditional composites. According to Tanaka and Goettler (2002) only several percent of clay by volume (vol.%) could increase the binding energy for nylon 6.6-clay. Increasing the binding energy could increase physical properties of polymer-clay nanocomposites.

Of these hybrid composites, polysulfone (PSF) as an organic matrix has been of special interest for its exceptional thermal and mechanical stability. Clay as a filler was obtained from South Lampung, Indonesia. The Clay were identified by XRD, consist of montmorillonite, chabazite, and cliptonilolite. Composition of clay were 3, 4, 5, and 6 wt.% PSF. Calcination temperature were 300, 350, 400 and 450 ^{0}C. These hybrid materials can be readily prepared by using phase inversion. The effect of various compositions and calcination temperature of clay to membrane properties are discussed.

2. Experimental

2.1. Materials

Polysulfone (PSF), N.N-dimethylacetamida (DMAc), Polyethyleneglycol (PEG), Dextran T-500 (Mw 500,000), Fenol, Sulfuric acid, acetone were supplied by Merck. CV. Minamata South Lampung, Indonesia supplied Clay. PSF, DMAc, PEG and clay are materials for dope solution. Dextran T-500 with nominal average molecular mass 500,000, phenol, and sulfuric acid were used as materials for retention membrane characterization by colorimetric method.

2.2. Preparation of clay

Clay in size 100 mesh was dried at 110 ^{0}C for 5 h, and then calcined at 300-450 ^{0}C for 1 h in air.

2.2. Fabricated of polysulfone clay membrane hybrids

Dope solutions were prepared at room temperature in the following way: in an Erlenmeyer dried placed 8.01 g DMAc, 2.25 g PEG, and 2.25 g PSF with vigorous stirring. Clay(without calcined) 3 wt.% PSF was added drop wise to solution slowly for overnight (15 h) with continues vigorous stirring. Others solution with several of clay composition 4, 5, 6 and 7 wt.% PSF respectively were prepared according to the same procedure. Addition of clay calcined carried out only for membrane with clay composition 5 wt.% PSF. All solution was kept at room temperature for 2 h in order to remove air bubble.

The solution was cast onto a glass plate by means of proper knife to form thin films. After casting, the films were immersed into coagulation bath of 25 ^{0}C to precipitate the polymer and form porous membranes. The phase inversion immediately started and the film peeled off the glass plate after some times.

2.3. Characterization of polysulfone-clay membrane

The surface morphology of the membranes was observed by scanning electron microscopy (SEM). The membranes were immersed at least overnight in such water and compacted at 1 atm for 30 minutes before being used in any experimental work. Stirred separated cell could hold a membrane disc of 23 mm in radius. Operating pressure of the cell was 1 atm. Permeation and retention experiment was carried out with distilled water and laboratory scale unit fed 1000 ppm of aqueous Dextran T-500. Permeate flux and retention was measured every 15 minutes. Permeation and retention of dextran was evaluated by colorimetric method.

3. Results and discussion

3.1. Effect of clay composition to performance of PSF-Clay membrane

The SEM images of PSF-clay membrane at composition 4, 5 wt.% PSF were shown in Figure.1 and 2.

Figure 1. SEM Morphology of PSF-C4 Membrane Surface (a) upper, (b) lower,(c) cross section

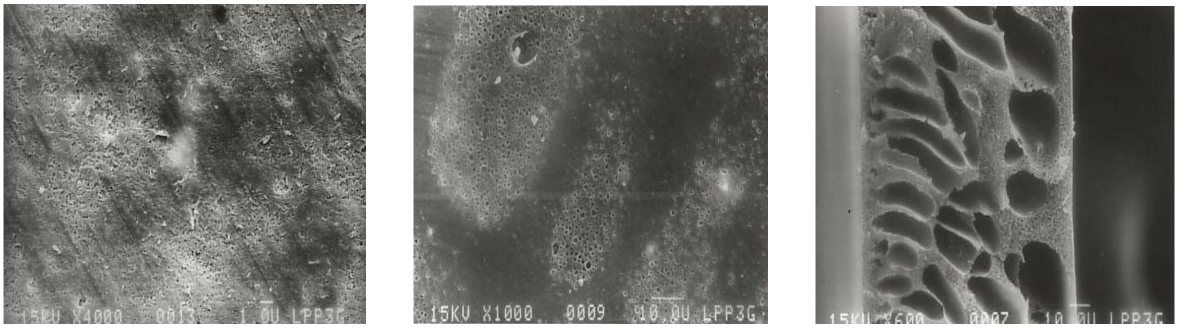

Figure 2. SEM Morphology of PSF-C5 Membrane Surface (a) upper, (b) lower,(c) cross section

The pore formation is started by adding water onto surface skin of solution. An incorporation of clay as silica phase into PSF matrix caused of increased amount of pore, and pore size of membranes (Figure.1 and 2). Because of clay is particle, which has pore, so membrane PSF-clay has pore too. Amount of pore and pore size could be affected to membrane permeability, not only these items but also pore size distribution could be affected too. Figure 1-2 show the actual photographs of pore formations of surface PSF-C4 and PSF-C5 membrane. Apparently, the SEM observed shown that amount of pore, pore size, and pore size distribution of membranes surface were not uniform. The more pore and the bigger pore size and pore size distributions of the membrane, the larger membrane permeability. Figure. 5 show permeability of pure water and dextran T-500 due to addition of clay into PSF matrix. An incorporation of clay into PSF matrix at 3 up to 6 wt.% PSF increased pure water and dextran T-500 flux about 109.81-381.56 % and 55.98-289.99 % respectively. Exception for PSF-C4 membrane, increasing of permeability could increase of rejection about 27.76-39.44%.

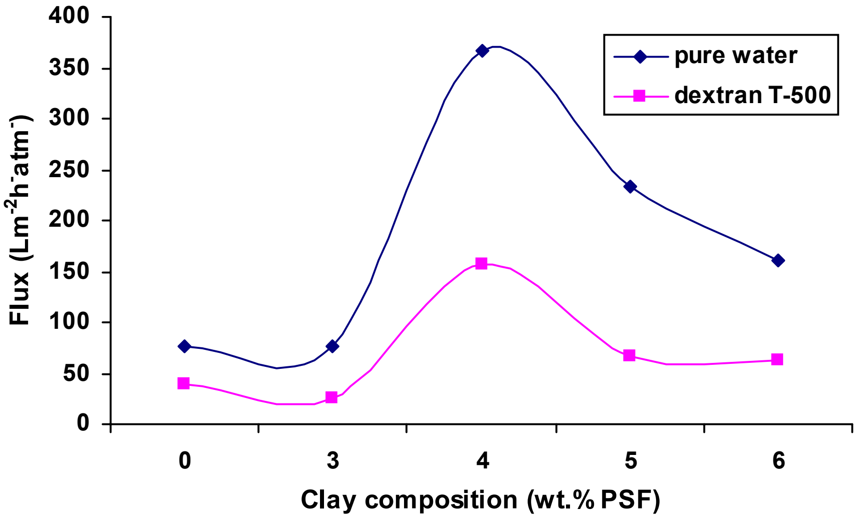

Figure 3. Effect of clay composition of PSF-clay membrane to pure water and dextran T-500 permeability

The increasing of these membranes permeability is not linear to increasing of the clay composition. In this case, addition of clay into PSF matrix at 4 wt. % PSF shows the highest membrane permeability. The result was caused of this condition reached in equilibrium composition, so amount of pore, and pore size larger than the others compositions. The others side, pore size distribution of membranes more uniform than the others. Figure 1 and 2 show clearly that the clay could not distribute in the membrane surface uniformly. Clay Distribution smaller in the upper parts than the lower parts of membranes (Figure.1a-b), so in the lower parts of membranes has more pore, larger pore size and pore size distribution more uniform than the upper parts. Its mean that the clay was precipitate in the lower part of membrane, indicated that clay not compatible yet in all side of PSF matrix.

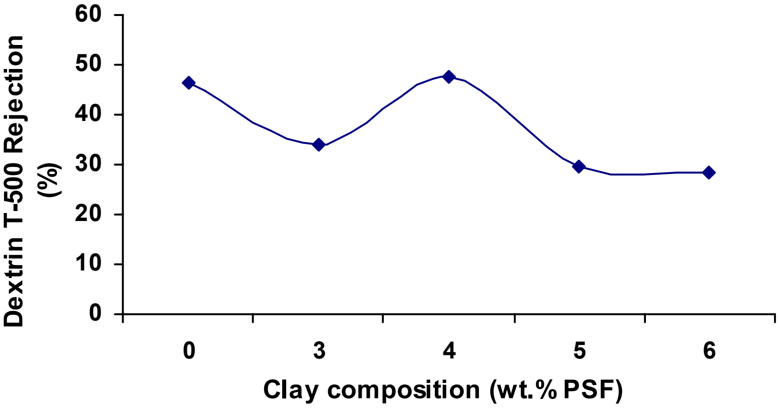

Figure 4. Effect of clay composition of PSF-clay membrane to rejection of dextran T-500

Figure. 6 show dextran T-500 rejection to various clay compositions. Membrane rejection decreased base on increasing of flux. This result showed that the membranes with various clay composition 4, 5, 6 wt.% PSF only could rejected the dextran T-500 about 33.85, 47.73, 29.76, and 28.38 % respectively. That means the retention of membrane for dextran T-500 still small.

3.2. Effect of calcinations temperature to PSF-Clay membrane performance

Figure. 5-6 shows the morphology of PSF-C5 membranes that were calcined at 300 and 400 ^{0}C.

Figure 6. SEM Morphology of PSF-C5.400 Membrane Surface (a) upper, (b) lower, (c) cross section

Apparently, the SEM observed showed that clay also randomly dispersed in PSF matrix. Due to this reason, amount of pore, pore size, and pore size distribution of membranes surface were not uniform. The pore diameter repeatedly changed in size due to temperature change. Based on this research, PSF-clay membrane have pore diameter about 2-10 nm, which indicates that PSF-clay membrane is of micro filtration type.

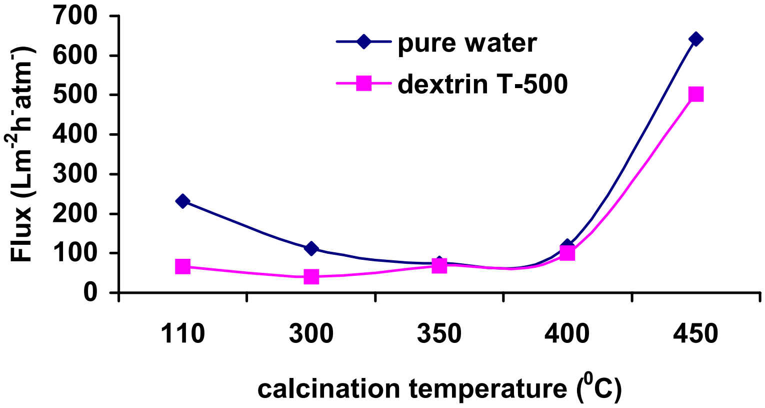

Figure 7. Effect of clay composition of PSF-clay membrane to pure water and dextran T-500 permeability

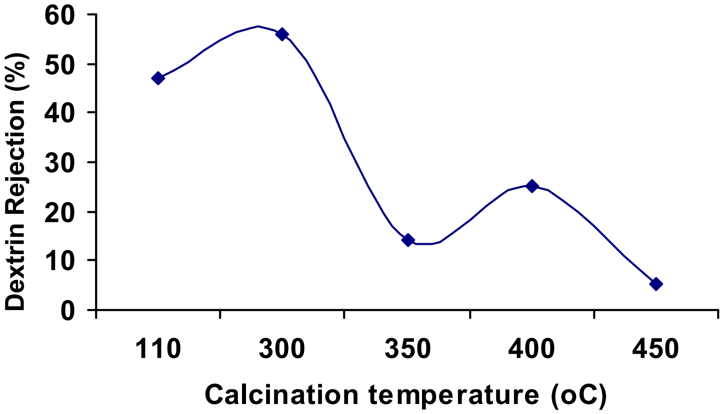

Figure 8. Effect of calcinations temperature of PSF-clay membrane to rejection of dextran

The result in Figure 7 and 8 also indicates that the changing of pore size when the calcinations temperature increased fluctuated. This fluctuation not only was caused by clay randomly dispersed, but also the clay was not compatible in PSF matrix. Pore size of the membrane become unstable, so calcinations probably could damage amount of membrane pore. This is the reason why the membrane permeability fluctuated depends on the calcinations temperature and pore membrane stability. Permeability of the PSF-clay calcined at 300 ^{o}C smaller than before calcined. On the other hand, permeability of PSF-clay increased when calcined at 450 ^{o}C. This result could affect to dextran rejection of the membrane, where calcined at 300 ^{o}C only increased of rejection about 16.32 % than before calcined. This result clearly that the clay calcined could not improved the membrane performance is like our expected.

4. Conclusion

Incorporating clay to PSF matrix membrane caused an increase in water permeability of membrane. Membrane permeability fluctuated depends on the amount of clay in PSF matrix and calcinations temperature of clay. Addition of clay into PSF matrix affected the porosity of membrane which caused an increase in permeability. In this result, the highest pure water and dextran permeability at clay composition 4 wt.% PSF, are 642.18 $Lm^{-2}h^{-1}atm^{-1}$ for pure water, and 12.80-501.71 $Lm^{-2}h^{-1}atm^{-1}$ for dextran T-500. The increasing of permeability leads to decreasing rejection of dextran. Although not for all temperature, clay calcined at 300 ^{o}C could increase dextran rejection by 16.32 % than before calcined. Based on pore size, the type of this membrane is micro filtration

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References

[1] H.-H. Huang, B. Orler, G.L. Wilkes, Structure-property behavior of new hybrid materials incorporating oligomeric species into sol–gel glasses. Part 3. Effect of acid content,tetraethoxysilane content, and molecular weight of polydimethylsiloxane, Macromole- cules 20 (1987) 1322–1330.

[2] S. Kohjiya, K. Ochiai, S. Yamashita, Preparation of inorganic/ organic hybrid gels by the sol–gel process, J. Non-Cryst. Solids 119 (1990) 132–135.

[3] A. Morikawa, Y. Iyoku, M. Kakimoto,Y. Imai, Preparation of a new class of polyimidesilica hybrid films by sol–gel process, Polym. J. 24 (1) (1992) 107–113.

[4] L. Mascia, A. Kioul, Polyimide-silica hybrid materials by sol–gel processing, J. Mater. Sci. Lett. 13 (1994) 641–643.

[5] J.H. Kim, Y.M. Lee, Gas permeation properties of poly(amide-6-*b*-ethylene oxide)-silica hybrid membranes, J. Membr. Sci. 193 (2001) 209.