Fabrication and characterization of hydroxyapatite based cow bone polysulfone mixed matrix membrane

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Abstract. In this work, polysulfone (PSf)/hydroxyapatite (HAp) mixed matrix membrane were prepared by using phase inversion technique for ultrafiltration application. The prepared PSf/HAp mixed matrix membrane were characterized in term of morphological and physicochemical properties by using SEM, contact angle measurement, membrane tensile measurement and membrane porosity. Meanwhile the performance of PSf/HAp mixed matrix membrane was conducted in term of pure water flux (PWF) by using permeability machine. The surface morphology of the MMMs showed the increasing pore number and size as the concentration of HAp increase. The increment weight ratio of the HAp in PSf membrane enhanced the membrane water flux from 113.44 L/m².h.bar to 228.13 L/m².h.bar due to increased porosity of the membrane. Meanwhile, the strength of the membrane was increased from 3.82 MPa to 5.2 MPa as HAp increases from 0 to 1.0 wt. % and decreased to 2.49 MPa at 1.5 wt.% HAp. This study suggested that HAp is a promising candidate as additive that can improve PSf membrane performance.

Keywords: polysulfone; hydroxyapatite; mixed matrix membrane; fabrication; polymer membrane; phase inversion

1. Introduction
Water covers 70% of the world and it is essential to the whole living things. But, nowadays the world faces a severe global crisis especially lack of fresh and clean water. In addition, in this new globalization, the increasing population, urbanization, changes of climate and inefficient management
are the reasons that lead to the scarcity of freshwater globally. As being reported by The Global Risks Report (2019), the under supply of freshwater has been acknowledged as one of the largest global risks in term of potential impact over next decade [1]. Surface and ground water were assessed as adequate freshwater resources but industrialization has pushed the mankind to meet the increasing demand of water, uncover the wastewater as one of the valuable additions to the existing fresh water resources [2]. There are many conventional methods for wastewater treatment such as coagulation and flocculation, ion exchange, adsorption and etc.

Membrane process is currently used in several ways to treat wastewater from contaminant and to produce clean water as the growing need for fresh water around the world. Membrane process is a filtering method driven by a force which is pressure and it is a process that affected by the pore size of the filter [3]. Membrane is divided into several separation process which are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). Ultrafiltration commonly used to filtrate the contaminants from polluted water and the most suitable method for heavy metal removal because of the pore size range that is between 2-100nm [4]. UF can achieve more than 90% of removal efficiency with a metal concentration ranging from 10 to 112 mg/L at pH ranging from 5 to 9.5 and at 2–5 bar of pressure [5].

These days, polymeric membrane is getting attention from the researchers due to its high resistance in several aspects such as temperature and chemical. Polymer is widely used to modify the physicochemical properties of the membrane in order to increase the rejection performance [6]. Polysulfone (PSf) membranes are the most common membranes used in membrane process due to its mechanical robustness and structural and strong chemical stability [7][8]. In addition, PSf, as a resin material, is now widely used as the raw material for ultrafiltration membrane fabrication due to its outstanding mechanical properties, great chemical resistance, good thermal stability and wide pH operation range [9]. However, PSf has hydrophobic nature and susceptible towards fouling problems that can lead to the low production of flux [10]. To overcome this, embedding additive like inorganic particles to produce mixed matrix membranes (MMMs) is said to be the promising method to increase the productivity and quality of the polymer membrane [11]. Incorporation of inorganic additive into polymer matrix could provide the desired properties in the membrane such as high selectivity and high mechanical, chemical and thermal strength [12][13].

Hydroxyapatite (Ca10(PO4)6(OH)2), a member of the apatite mineral, can be used for heavy metal remediation in water treatment [14]. Hydroxyapatite (HAP) consist a special chemical property that can tolerate substitution of metal cation and oxyanion in the structure at Ca2+ and PO43- position resulting in the toxic ions being removed from waste water [15]. Due to several characteristics such as low cost, non-toxic and high potential adsorption of heavy metal ions, HAp is a promising material as an adsorbent to remove contaminant in waste water [14][16][17]. In this work, fabrication of mixed matrix membranes (MMMs) PSf/HAp ultrafiltration membrane was prepared via phase inversion technique. The role of HAp for improving the hydrophilicity of the polysulfone UF membrane is discussed.

2. Materials and methods

2.1. Materials
The cow bone waste were bought from a local butcher in Batu Pahat, Johor, Malaysia. Polysulfone (UDEL P-1700) purchased from Solvay, N-Methyl-2-Pyrrolidone (NMP) and polyvinylpyrrolidone (PVP) purchased from MERCK were used as polymer, solvent and pore forming agent, respectively. Distilled water used for coagulation bath.

2.2. Preparation of Hap powder
HAp were made from waste cow bones and the synthesize method were referred from [18]. The waste cow bones were crushed manually into smaller pieces. The bones then were boiled in 100°C hot water
to remove excessive tissues and fats. Then, the bones were dried in oven at 100°C at 24 hr. After drying, the bones were crushed and calcined in furnace (Magna V) at 800°C for 3 hr with the heating rate of 10°C/min. The temperature of the furnace were cooled down to room temperature at 10°C/min. After calcination process, the bones were milled into powder using planetary ball mill. The final powder were sieved to obtain powder size below than 20μm.

2.3. Membrane preparation

The fabrication of PSf/HAp membrane were done using phase inversion method referred from [19]. Table 1 shows the composition of the casting solution for five membranes with different mass ratio of polymer and HAp powder.

| Sample | HAp (wt.%) | PSf (wt.%) | PVP (wt.%) | NMP |
|--------|------------|------------|------------|-----|
| 1      | 0          |            |            | 84  |
| 2      | 0.5        |            |            | 83.5|
| 3      | 1.0        | 15         | 1          | 83  |
| 4      | 1.5        |            |            | 82.5|
| 5      | 2.0        |            |            | 82  |

The flat-sheet membranes were prepared by dissolving PVP with NMP under gentle agitation. HAp powder were latter added and stirred for 6 hours to allow uniform dispersion of the powder in the solution. Lastly, the PSf pelletes were gradually added and suspension were stirred with heat 60°C until solution completely homogenous. After that, the casting solution was poured into bottle and was degassed using sonicator for 1 hour to release the bubbles. After the bubbles completely released, the dope solution was cast on a glass plate using a glass rod at room temperature and placed in coagulation bath to form a sheet of membrane due to the induction of non-solvent. The flat-sheet was then removed from coagulation bath and was dried in room temperature for 24 hour.

2.4. Characterization of MMMs

The morphological properties of MMMs were characterized using JEOL JSM-6380LA scanning electron microscope (SEM) in which cross-sectional samples were initially fractured in nitrogen liquid before being spur-coated with gold, Au to enable the electron interaction with atoms in the samples. Analysis on water contact angle of membranes is necessary to determine the hydrophilicity of the membrane surface. Contact angle goniometer (IMC-159D, Imoto Machinery, Japan) with sesile drop technique was used to measure the water contact angle of the membrane. Deionized water was used as the liquid and measurement were done at 15 different location to derive an average value of water contact angle.

Tensile strength using Universal Tensile Machine with design code of D882-12 as standard tensile test referred from American Society of Testing at the strain rate of 5 mm/min. The membrane were cut into strips 5 cm long and 1 cm wide. The vernier calipper was used to measure the thickness of the membrane. At least 3 samples measurement were carried out to derive the average value.

In order to measure overall porosity, the flat-sheet membrane were cut with same length (around 2 cm). Then, the membrane were immersed in the distilled water for 24 hr. After 24 hr, the membrane were taken out from water and the excess water on the membrane surface were removed by blotting with tissue paper. The weight of wet membrane were recorded before being dried in oven at 50°C for 24 hr. The dried membrane were then being measured by analytical balance. For the measurement of the overall porosity of each sample, Equation 1 was employed.
where $\rho_{w}$ is density of pure water at room temperature ($g/cm^3$) and $v$ is the volume of membrane in wet state ($cm^3$).

Pure water flux analysis was determined by an ultrafiltration cross-flow permeation testing unit feed with distilled water at pressure 2 bars. The pure water flux (PWF) will be measure by direct measurement of the permeate flow using Equation 2:

$$PWF = \frac{Q}{A \times \Delta T}$$  \hspace{1cm} (2)

where PWF is the pure water flux (L/m².h⁻¹), $Q$ is the permeate volume (L), $A$ is the membrane area (m²) and $\Delta T$ is the time (h).

3. Results and discussion

3.1. Characterization of MMMs

3.1.1. Scanning electron microscope

The morphological structure of the membrane were examined by SEM micrography analysis as shown in Figure 1. Generally, all membrane surface showed the dispersion of HAp powder over the surface despite of agglomeration denoted by the presence of lump in certain area. The agglomeration can be defined that the HAp is naturally exists. From the figure, macrovoids also can be seen at some place among the finger-like structure of the membrane with 2.0 wt.% of HAp due to the agglomeration. The cross-section images seems to be similar for every membrane.

Therefore, the HAp additive did not have any particular influence in the MMMs morphology. However, the finger-like structure in MMMs are suprisingly more larger than the control membrane. This situation might be due to the addition HAp in MMMs. In general, asymmetrical structures were achieved for all membranes, consisting of a thin dense layer supported supported by a finger-like. This situation has common in SEM image result reported by [20]. It has been reported by [21] that the use of more additive than the suitable amount could resulted in pore blocking in the membrane and resulting in low water flux due to agglomeration of particles.

The surface of the membrane showed that the increasing number of pores from the controlled membrane to the 2.0 wt.% HAp. The increasing number of pores will increase the surface porosity. Increasing porosity will increase the water flux hence, producing higher permeate [22].
3.1.2. Contact angle analysis

Contact angle is a method that used to measure the surface wettability and to describe the hydrophilicity of the membrane. The higher the hydrophilicity of the membrane, the lower the value of contact angle. Figure 2 shows the value of contact angle for all samples based on HAp content. The result obviously showed that the contact angle decreased as the concentration of HAp increased from 0.5 to 1.5 wt.% which is 80.1° to 65.5° and slightly increased at HAp concentration 2.0 wt.% which is 67.2°. This increasing occurrence could be due to the presence of additive that has lowered down the surface tension of the PSf cause the water easily spread and attracted to the membrane surface [23]. The increasing hydrophilicity of the membrane might cause by the surface enrichment of hydroxyl group [19]. In this case study, HAp consist hydroxyl group that can enhance the hydrophobicity of the PSf membrane. Meanwhile the decreasing contact angle might be caused by the agglomeration of the HAp particles among the surface of the membrane. As a result, the surface (contact) area of the hydrophilic functional groups possessed by additive is reduced, hence, cause the hydrophilicity of the membrane surface decreased [24].

**Figure 1**: SEM images of cross section (left) and top surface (right) of membranes
3.1.3. Tensile strength analysis

Tensile strength analysis is used to measure the strength of the membrane with the addition of inorganic additive. The tensile analysis revealed that the membrane tensile is increased from the control membrane to membrane with 1.0 wt.% HAp and increased from 3.82 MPa to 5.2 MPa as being shown in Figure 3. However, the tensile analysis dropped at membrane with 1.5 wt.% HAp with 2.44 MPa and increased back at 2.0 wt.% HAp with 4.40 MPa. The unstability in tensile analysis might due to the structure of the membrane resulting from porosity [25]. In addition, the increasing pore also reducing the mechanical strength [26].

![Figure 3: Tensile strength (MPa) with different wt.% of HAp particles.](image-url)
3.1.4. Porosity analysis
Membrane porosity can be defined as weight or pure water trapped in 1 m³ of membrane structure [27]. Porosity is an important analysis for membrane separation because it determines the performances and properties [28]. Figure 4 demonstrated the porosity data of the prepared membrane at different concentration of HAp. The result shows that the porosity increased proportionally to the HAp concentration. These results were in line with the increase of hydrophilicity properties (via hydroxyl group in HAp) that can be seen by the large finger-like structure of MMMs than the controlled membrane [20]. However, the data for 2.0 wt.% HAp shows that the porosity value decreased. This situation can be explained due to agglomeration of HAp that occur in the finger-like structure of the membrane that cause the pore is blocked by the excessive HAp particles [21]. The increasing of solution viscosity that resulted in delaying the liquid-liquid exchanging process attributed to produce a thicker and low porosity membrane [29].

![Figure 4: Porosity of PSf membrane with wt.% of HAp particles](image)

3.2. Water permeation flux
Figure 5 shows the result of pure water flux for each membrane. As demonstrated in the figure, the membrane flux significantly improved by the addition of HAp as additive. The PWF increases constantly from 0 wt.% to 1.5 wt.% of HAp which is from 113.44 L/m².h.bar to 228.13 L/m².h.bar. The result of PWF is in agreement with the contact angle result that conclude by adding inorganic additive HAp with increasing concentration at each membrane, the hydrophilicity can be improved which definitely affect the PWF value. The PWF value is also raised by the increasing number of pores induced by the increasing concentration of HAp in MMMs, which is in line with the increasing porosity [30]. The PWF value also corresponding to the finger-like structure in SEM observation that become larger as the concentration of HAp increased. However, the PWF decreased at concentration 2.0 wt.% and this situation might be caused by the HAp particles that creates agglomeration among the finger-like structure of the membrane and lead to pore blocking that prevent the water from flowing. The result was in line with study done by [31] and [21] about effect of inorganic additive concentration on PWF.
Figure 5: Permeation water flux result

4. Conclusion
In this study, flat-sheet PSf/HAp mixed matrix membranes were prepared via phase inversion technique were investigated. The effect of HAp as inorganic additive into membrane formulation for surface enhancement were observed. In addition, the morphological structures, hydrophilicity properties, porosity, tensile strength and pure water fluxes were also studied. The incorporation of HAp has been confirmed by SEM analysis that illustrates typical asymmetrical structures of the membrane. An agglomeration of HAp has been identified at certain part of membrane. Despite the agglomeration of HAp within the membrane, pure water flux analysis showed that membrane with 1.5 wt.% of HAp gives the highest permeate with 228.13 L/m².h.bar due to increasing number of pores. Corresponding with the increment of the fluxes, the porosity of each membrane sample also increases proportional to the HAp concentration. Meanwhile, the mechanical property of tensile strength was found to increase from 3.82 MPa to 5.20 MPa as the concentration of HAp increase from 0 wt.% to 1.0 wt.% and decrease at 1.5 wt.% The addition of inorganic additive into the membrane formulation attribute to the surface enhancement of PSf membrane which is increase the hydrophilicity of the membrane. Contact angle data for 1.5 wt.% of HAp gives the lowest result which is 65.5° than the control membrane. It can be concluded that the presence of inorganic additive HAp has improved the hydrophilicity of PSf membrane.

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