SHEAR RATE EFFECT ON ASYMMETRIC KAOLIN-POLYETHERSULFONE HOLLOW FIBRE MEMBRANE

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ABSTRACT

Inorganic hollow fibre membrane is normally made from premium ceramics which is not easy to procure. Furthermore, the process of producing ceramic membrane requires the ceramic precursor to undergoes sintering process at high temperature. Thus, the cost of developing a ceramic membrane using experimental method is expensive. Kaolin have been identified as an alternative ceramic material while offering reasonable cost. However, knowledge on kaolin as base material for hollow fibre membrane are still in its infancy and much are not yet known. Thus, this study aims to produce asymmetrical Kaolin/Polyethersulfone (PESf) hollow fibre membrane with thin outer finger-like region by observing shear experience within the spinneret in relation to hollow fibre formation and morphology. The research work is executed in three phase; kaolin solution formulation, spinning and characterization, CFD simulation. Kaolin solutions formulated using Polyethersulfone (PESf) as binder and N-methyl-2-pyrrolidone (NMP) as solvent were rheologically assessed using a rotational viscometer to obtain the values of power law coefficients, *n* and *k*. These rheological data are then correlated with the characteristic of the hollow fibre membrane, essentially hollow fibre morphology and porosity. The shear rate inside the spinneret annulus is obtained using computational fluid dynamics (CFD) method. Rheology investigation shows that Kaolin suspension exhibits non-Newtonian behavior under the power law scheme. An increase in the Kaolin/PESf ratio further increases the viscous behavior of the non-Newtonian liquid. The power law coefficients for the Kaolin suspension were successfully determine and is used in the computational fluid dynamic analysis. Morphology study on spun hollow fibre shows asymmetric structure. The study also indicates that there is a strong link between extrusion shear to precipitation rate. It is found membrane spun at low shear experience of 109.55 s^{-1} have thin outer finger like region at 24% area ratio and porosity of 68%. Increasing the shear experience in the annulus outer wall; affects the apparent viscosity and ultimately causing the precipitation rate to increase and grows the outer finger-like region. At shear experience of 2155.78 s^{-1}, outer finger like region is at 48% and membrane porosity at 48%. This study established that rheology characteristic of the kaolin suspension plays an important role to the shear experience behavior in the spinneret annulus. Ultimately, correlation of the shear experience and hollow fibre morphology enable us to predict hollow fibre performance in the design process reducing the overall development cost.

ABSTRAK

KESAN RICIH KEPADA MEMBRAN GENTIANG GERONGGANG KAOLIN-POLYETHERSULFONE

Membran gentian geronggang tak organik biasanya dibuat daripada seramik yang berharga dansusah untuk didapati. Tambahan pula, proses untuk menghasilkan membrane seramik memerlukan proses pembakaran asas seramik membran pada suhu yang tinggi. Justeru itu, kos untuk membangun membrane seramik secara kaedah ujikaji adalah mahal. Kaolin telah dikenal pasti sebagai bahan seramik alternatif dan menawarkan kos yang berpatutan. Walau bagaimanapun, pengetahuan mengenai kaolin sebagai bahan asas untuk membran gentian geronggang masih di peringkat awal dan belum diterokai sepenuhnya. Oleh itu, kajian ini bertujuan untuk menghasilkan membrane gentian beronggang berasaskan Kaolin / Polyethersulfone (PESf) dengan bercirikan rantau jejari luar nipis dengan memerhatikan pengalaman ricih dalam spinneret serta kaitannya dengan pembentukan serat berongga dan morfologi. Kerja-kerja penyelidikan projek ini dilaksanakan secara tiga fasa; penggubalan cecair kaolin, penghasilan gentian dan pencirian, analisa data simulasi. Cecair Kaolin dirumuskan menggunakan Polyethersulfone (PESf) sebagai pengikat dan N-metil-2-pyrrolidone (NMP) sebagai pelarut dan pencirian kelikatan dinilai menggunakan meter kelikatan untuk mendapatkan nilai pekali hukum kuasa, n dan k. Data-data reologi kemudiannya dikaitkan dengan ciri-ciri membran gentian geronggang, terutamanya morfologi serat dan tahap keliangan. Kadar ricih dalam anulus spinneret diperolehi menggunakan kaedah pengiraan dinamik bendalir berkomputer (CFD). Siasatan reologi menunjukkan cecair campuran kaolin mempamerkan kelakuan cecair bukan Newtonian dengan skim persamaan bendalir kuasa. Peningkatan nisbah Kaolin/PESf seterusnya meningkatkan kelakuan kelikatan cecair bukan Newtonian ini. Pemalar persamaan bendalir untuk cecair kaolin dalam ujikaji ini telah berjaya ditentukan dan digunakan dalam analisis pengiraan dinamik bendalir (CFD). Kajian morfologi ke atas hasil membrane gentian geronggang menunjukkan struktur berbentuk asimetrik. Kajian ini menunjukkan terdapat kaitan yang kuat diantara penyemperitan ricih dan kadar pemendakan. Di dapati, membrane geronggang yang dihasilkan pada keadaan ricih rendah 109.55 s^{-1} mempunyai lapisan struktur jejari luar yang kecil pada 24% dan kadar keliangan 68%. Peningkatan penyemperitan ricih pada dinding annulus memberi kesan kepada kelikatan cecair seterusnya menyebabkan kadar pemendakan meningkat. Ini menyebabkan struktur jejari luar membesar. Pada keadaan ricih 2155.78 s^{-1}, nisbah struktur jejari luar ialah 48% dan kadar keliangan pada 48%. Kajian ini merumuskan bahawa sifat reologi cecair kaolin memainkan peranan penting kepada keadaan ricih cecair di dalam anulus spineret. Seterusnya, dengan mengaitkan kejadian ricih dan morfologi gentian geronggang; ia membolehkan kita untuk meramal prestasi membran ketika proses rekabentuk disamping mengurangkan kos pembangunan.

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LIST OF ABBREVIATIONS

AFM - Atomic force microscope

CFD - Computational fluid dynamics

CR - Centre region

DG - Diethylene Glycol

ID - Inside diameter

IR - Inner region

NMP - N-methyl-2-pyrrolidone

OD - Outside diameter

OR - Outside region

PESf - Polyethersulfone

SEM - Scanning electron microscope

LIST OF NOMENCLATURES

u - Fluid velocity

ρ - Fluid density.

S_i - Mass-distributed external force per unit mass.

g_i - Gravitational component.

h - Thermal enthalpy.

Q_H - Heat source or sink per unit volume.

τ_{ik} - Viscous shear stress tensor.

q_i - Diffusive heat flux.

μ - Dynamic viscosity coefficient.

K - Liquid consistency coefficient.

n - Liquid power law index.

τ_0 - Liquid yield stress.

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CHAPTER 1

INTRODUCTION

1.1 Overview

A membrane can be defined as a conventional filter with finer mesh or much smaller pores to separate tiny particles or molecules (Cui and Muralidhara, 2010). It can be described as a perm-selective barrier or a fine sieve, which under the effect of a transfer force, will allow or prohibit the passage of certain components between two separate mediums. Membrane systems were discovered naturally in the form of biological membranes. This led to development of synthetic membranes for industrial use, which had been strongly developed since the second half of the last century. Membrane technology is widely used for water management and many other industrial applications such as food, beverage, bioreactors, and pharmaceutical industry.

It is estimated that worldwide sales of membranes and modules were at an astounding value of US$4.4 billion back in 1988. Of those figures, Haemodialysis/filtration process tops the chart with the highest sales for both membrane processes and applications. Sales data also shows that the largest growth for type of membrane application goes to gas separation process at an annual rate of 15% per annum. Sales records also show that the total sales of membrane product would likely to grow at a rate of more than 8% (Strathmann, 1999). This is further corroborated by another published study (Nunes and Peineman, 2006), which states that the combined market for membranes used in separation and non-separation applications to be worth $5 billion in the US alone, with an annual growth rate of 6.6%. The demand for pure water around the world also drives the market for cross-flow membrane equipment and membranes world-wide from $6.8 billion in 2005 to $9 billion in 2008. These figures show how the membranes industry advances through the years and shows great potential in the coming years.

The mechanism behind a membrane separation process is the pressure difference between a porous layer. The membrane separation of a mixture is achieved by rejecting at least one component of mixture while passing other component through the membrane due to size exclusion. The flow of the feed is divided into two; retentate and permeate flow. The retentate flow is the stream with compositions of both the components that are rejected by the membrane and a quantity of components that can pass through the membrane but does not has the chance to pass through. While the permeate flow is the stream that are passed through the membrane. According to Cui and Muralidhara (2010), the compositions of permeate are of the particles and molecules of less or smaller size compared to the membrane's pores.

Membrane application can also be categorized by the membrane pore size; a membrane with a pore size at 0.3 – 1 nm is normally use for gas separation process, as the pore size decreases in size the separation capability also increases which enables Nanofiltration, Ultrafiltration and Microfiltration process took place (Rijn, 2004). A Microfiltration membrane which have 50 nm – 5 5 μm in pore size is used in wide variety of application such as water treatment, sterile filtration and bacteria screening.

Two types of membrane material are available; organic and in-organic membranes. Organic membrane is usually made up of various polymers such as polyethersulfone (PESf) and polyvinylidene fluoride (PVDF). Polymer membranes are widely available as it was commercially developed earlier by chemical companies (Dupont, Monsanto, Dow) during the 1960s and 1970s (Roman, Ubersax, and Fleming, 2001). The membranes are relatively easier to be applied to different types of configuration and lower production cost compared to competing alternative.

There are three types of polymers suitable to be use as membrane material; crystalline, glassy and rubbery polymers (Robeson, 1999; Stern, 1994). Glassy polymers offer the best characteristic in the gas separation industry as it has good permeability/selectivity combination and mechanical properties. Crystalline polymers are less permeable while rubbery polymers have poor selectivity.

After decades of research and development of polymer membranes, it appears that significant advance on traditional polymer membranes is difficult to attain. For instances, the separation factor for a pair of gas is related to the permeability of the gas up to a certain limit; any further improvement in the gas separation performance will require different type of materials (Robeson, 1991; Roman *et.all*, 2001). New demand for membrane process conditions and applications requires membranes with improve temperature and chemical resistance, which polymer membranes are known to have limited performance due to its organic nature.

On the other hand, inorganic membrane possesses characteristic that is desirable at certain membrane processes compared to polymer membrane; temperature and wear resistances, resistive to water, thermally stable, chemically resistant, and durable (Rijn, 2004; Nezahat, Ilknur and Ahmet, 2015). The inorganic properties contribute to better membrane performances and alternative cleaning method which is normally not possible on a polymeric membrane thus giving longer lifespan. Thus, many studies were done in early 1980s to investigate inorganic membrane performance for separation purposes (Keizer and Verweij, 1996).

A ceramic membrane can be used as a support for a thin layer of a separating surface. It provides strength while the porous structure gave low resistance to fluid flow. The starting material for ceramic membrane support is normally made from Alumina (AL_2O_3), cordierite ($Mg_2Al_4Si_5O_{18}$) and mullite ($Al_6Si_2O_{13}$). However, it is known that ceramic membrane is brittle and expensive to produce. (Cui and Muralidhara, 2010; Liu and Li, 2005; Nezahat *et.all*, 2015).

1.2 Problem Statement

Production of inorganic-ceramic membrane by the industry are limited due to several reasons. The price for starting material of a ceramic membrane is expensive and additional sintering process is required to produce a porous structure, thus numerous effort has been made to find alternative material that is cheaper while having same if not better properties (Guechi, Harabi, Condoum, Zenikheri, Boudaira, Bouzerara and Foughali, 2015; Bouidara, Abdelhamid, Bouzerarra, Zenikheri, Foughali and Guechi, 2015; Silva, Lira, Lima and Freitas, 2014). Low cost raw clay and kaolin is considered as a good alternative to ceramic material for membrane support since that it is cheaper than premium ceramic material (Khider, Akretche and Larbot, 2004). Kaolin ($Al_2Si_2O_5(OH)_4$) is available in abundance, cheap and quite common in the industry for several practical uses; pharmaceutical, paper, ink and the construction industry. Studies show that the material has desirable characteristic for membrane support alternative as it is easy to handle, fine texture, white colored, low shrinkage, thermally and chemically stable (Mohammadi and Pak, 2003). Compared to metal oxide material, the sintering temperature is also lower which translate to lower manufacturing cost (Guechi *et.all*, 2015). Several studies have been made on Kaolin and its performances as an alternative starting material for membrane support. The material is stable enough that it can be used alone or mixed with other ceramic materials such as alumina, dolomite and kieselgur for porosity improvement (Bouzera, Harabi, Achour and Larbot, 2006; Chen, Qi, Xing and Nu, 2008; Dong, Lin, Xie, Wang, Ding, Fang, Liu and Meng, 2009).

Study of kaolin as alternative cheap material are more inclined to membrane support in the shape of flat sheet and tubular structure (Bouzera *et.all*, 2006; Mohammadi and Pak, 2003). On the other hand, little information can be found on kaolin support in the shape of hollow fibre configuration. Hollow fibre membrane is normally produced using phase inversion technique which requires the material to be in a polymeric (non-aqueous) suspension. The fabrication process is known as spinning process involve three major steps; material preparation, spinning process and sintering process. Zykamilia Kamin (2011) have reported of producing hollow fibre membrane using Kaolin/PESf. Her study concentrates on the effect of the fabrication variables such as material ratio, spinning parameters and the effect of sintering temperature on the fibre morphology. An important step in the fabrication process that largely influenced the final morphology of the hollow fibre support is the spinning variables and the design of the spinneret. These variables are interrelated and any change in one of the variable affect the hollow fibre morphology.

Studies on the effect of the spinning process parameters and spinneret geometry for polymeric membrane are widely available and well establish. Several researchers have emphasized the importance of understanding the spinning parameters and spinneret design; they were able to produce defect free, optimized spinning process and ultimately reduce the production cost of hollow fibre membrane (Chung and Xu, 1998; Qin, Wang and Chung, 2000; Qin, Gu and Chung, 2001; Cao, Chung, Chen and Dong, 2004; Wang, Matsuura, Chung and Guo, 2004; Ren, Wong and Li, 2005). However, studies on ceramic hollow fibre spinning specifically on Kaolin/PESf material is still lacking. To the best knowledge of the author, the study on the effect of shear rate variance due to extrusion rate through spinning on Kaolin/PesF hollow fibre performance is not yet available. Although studies on the effect of shear rate on polymeric hollow fibre membrane have been establish, findings deduce from those studies are of limited use due to difference in fabrication process (sintering) and material properties. Thus, it is important to extend the knowledge base on the effect of the extrusion rates to the morphology of the Kaolin/PESf hollow fibre membrane. Consequently, enable us to predict spinning condition suitable to produce asymmetric membrane with thin outer layer.

1.3 Research Objective

The main objective of this research is to produce an asymmetrical kaolin/ Polyethersulfone (PESf) hollow fibre membrane with thin outer finger-like region through the study of shear experience within a spinneret in relation to hollow fibre formation and morphology. The objectives of the study are;

1) To investigate the rheology of Kaolin/Polyethersulfone (PESf) suspension at Kaolin/PESf ratio of 1, 1.5 and 2.

2) To produce Kaolin/PESf hollow fibre membrane using spinneret with two different annulus design; straight and conical.

3) To simulation the shear rate in the spinneret annulus at different extrusion rate using Computational Fluid Dynamics (CFD) method in a straight and conical spinneret.

4) To study the influence of shear in the spinneret annulus wall caused by extrusion and different annulus construction (straight/conical) to the morphology of hollow fibre membrane.

1.4 Scope of Research

This research is conducted in the field of membrane study. The membrane in which is characterized under this study is Kaolin; an alternative material to produce inorganic membrane in hollow fibre configuration. In this research, kaolin suspension was formulated from Kaolin as base material, PolyetherSulfone (PESf) as binder and NMP as solvent. Wet spinning procedure was used to produce the asymmetric hollow fibre structure using two different spinneret design; straight and conical shape. The extrusion rates, viscosity of Kaolin suspension and design of spinnerets were treated as input spinning parameter variables. The morphology and computational fluid dynamics data output were treated as the output response and were studied. Computational fluid dynamic method is used to study the flow field in greater detail on each spinneret design while Scanning Electron Microscopy (SEM) and porosity study were used to study hollow fibre precursor morphology. This research work is limited to study the effect of spinning parameters and spinneret design to hollow fibre morphologies by utilizing CFD method and consequently the ability to predict hollow fibre membrane properties.

1.5 Significance of research

Completing this research makes significant contribution in the field of membrane technology both in the industry and academia.

a. Kaolin as an alternative cheap material to be used as hollow fibre membrane support compared to other ceramic membrane which is made from premium material.

b. Literature have shown that significant findings have been made on the effect of extrusion rates to polymer base hollow fibre morphology. However, this research is the first work to study the flow field in a spinneret nozzle at a greater detail and correlating the data to inorganic hollow fibre membrane morphology.

c. The ability to predict hollow fibre membrane performance based on CFD data in the design phase significantly reduce production cost while minimizing waste.

1.4 Thesis outline

Chapter 1 gave the overview information on membrane technology and its challenges. This chapter covers type of membrane, membrane material and critical problem in ceramic hollow fibre development. The objective of the study is defined in this chapter.

Current technology and research trend in ceramic hollow fibre membrane is carried out in chapter 2. The scope of study includes ceramic membranes, materials, preparation of ceramic hollow fibre membrane, spinning parameters, and sintering process.

Chapter 3 described the general methodology of the study, rheology investigation, spinneret design, hollow fibre spinning system and CFD study. The Kaolin suspension rheology properties is investigated as it is required in the CFD analysis. Kaolin hollow fibre membrane is prepared using wet spinning method to minimize the effect of other parameters on the morphology of the hollow fibre membrane.