การเปรียบเทียบเยื่อเลือกผ่านจาก ZSM - 5 และ POSS นาโนคอมโพสิตเพอแวปพอเรชันสำหรับการแยกของเฟอร์ฟูรัลและน้ำ

นายเศรษฐ สวัสดิรักษ์

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บทคัดย่อและแฟ้มข้อมูลฉบับเต็มของวิทยานิพนธ์ตั้งแต่ปีการศึกษา 2554 ที่ให้บริการในคลังปัญญาจุฬาฯ (CUIR)
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ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

COMPARISON OF ZSM - 5 AND POSS NANOCOMPOSITE PERVAPORATION MEMBRANES FOR FURFURAL/WATER SEPARATION

Mr. Seth Sawatdiruk

จุฬาลงกรณ์มหาวิทยาลัย
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A Thesis Submitted in Partial Fulfillment of the Requirements
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เศรษฐ สวัสดิรักษ์ : การเปรียบเทียบเยื่อเลือกผ่านจาก ZSM - 5 และ POSS นาโนคอมโพสิตเพอแวปพอเรชัน สำหรับการแยกของเฟอร์ฟูรัลและน้ำ (COMPARISON OF ZSM - 5 AND POSS NANOCOMPOSITE PERVAPORATION MEMBRANES FOR FURFURAL/WATER SEPARATION) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ดร. ชลิดา คล้ายโสม, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: ดร. ขจรศักดิ์ เฟื่องนวกิจ, 71 หน้า.

การแยกเฟอร์ฟูรัลออกจากน้ำนิยมใช้วิธีการกลั่นหรือการกัดโดยใช้ตัวทำละลาย ซึ่งเป็นกระบวนการที่ใช้พลังงานสูงหรือใช้สารเคมีเข้ามาเกี่ยวข้อง จึงมีความจำเป็นในการหากระบวนการแยกแบบอื่นที่ประหยัด ใช้พลังงานต่ำ ซึ่งระบบเพอแวปพอเรชันเป็นกระบวนการเยื่อเลือกผ่านที่ตอบโจทย์เหล่านั้น หากสามารถพัฒนาแผ่นเยื่อเลือกผ่านให้มีสมบัติที่เหมาะสม สามารถแยกเฟอร์ฟูรัลได้มีประสิทธิภาพสูงขึ้น จะสามารถนำมาใช้แทนกระบวนกลั่นและการสกัดได้ ดังนั้น ในงานวิจัยนี้จึงมุ่งเน้นพัฒนาแผ่นเยื่อเลือกผ่านเพื่อใช้ในการแยกเฟอร์ฟูรัลและน้ำให้มีประสิทธิภาพดีขึ้น โดยการเตรียมแผ่นเยื่อเลือกผ่านไดเมทิลไซลอกเซนประกอบแต่งด้วยสารเติมแต่งจาก zeolite socony mobil – 5 (ZSM – 5), octanitropheyl (ONPS) and octaaminophenyl (OAPS) ผลการทดลองพบว่า OAPS สามารถช่วยเพิ่มค่าประสิทธิภาพในการแยกสารให้สูงขึ้นเมื่อเทียบกับแผ่นเยื่อเลือกผ่านที่ผสมด้วย ONPS และ ZSM – 5 เนื่องจาก OAPS มีโครงสร้างที่แสดงความเป็นขั้วที่น้อยที่สุดซึ่งจะทำให้สามารถเกิดการเลือกจับกับสารเฟอร์ฟูรัลที่มีความเป็นขั้วต่ำกว่าน้ำได้ การเพิ่มปริมาณการใช้ OAPS สามารถช่วยปรับปรุงค่าประสิทธิภาพการแยกสารให้ดีขึ้น โดยเยื่อเลือกผ่านไดเมทิลไซลอกเซนที่ผสม OAPS ที่อัตราส่วน 15% โดยมวล สามารถแยกสารเฟอร์ฟูรัลได้ความเข้มข้นประมาณ 20% โดยมวล จากสารผสมตั้งต้นที่มีความเข้มข้นเฟอร์ฟูรัล 3% โดยมวล นอกจากนี้ การเพิ่มอุณหภูมิของสารป้อนจาก 30 ถึง 50 ยังช่วยเพิ่มค่าฟลักซ์และประสิทธิภาพในการแยกเฟอร์ฟูรัลเนื่องจากช่วยเพิ่มความดันไอของสารให้สูงขึ้น แต่เมื่อเพิ่มอุณหภูมิถึง 60 องศาเซลเซียส ประสิทธิการแยกสารลดลง เนื่องจากสายโซ่พอลิเมอร์

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SETH SAWATDIRUK: COMPARISON OF ZSM - 5 AND POSS NANOCOMPOSITE PERVAPORATION MEMBRANES FOR FURFURAL/WATER SEPARATION. ADVISOR: CHALIDA KLAYSOM, Ph.D., CO-ADVISOR: KAJORNSAK FAUNGNAWAKIJ, Dr.Eng, 71 pp.

The recovery of furfural via a conventional separation technology like distillation and solvent extraction requires very large energy consumption and high amount of chemical solvent. Thus, there is a need for an alternative separation process that is economic and more energy friendly for the furfural recovery. Pervaporation is a well - recognized energy friendly and effective separation tool. If there is suitable pervaporation membrane with efficient separation performance, the pervaporation can be a promising replacement for the conventional separation method. Therefore, this thesis aims to develop a suitable membrane for furfural recovery via pervaporation process. In this work, the polydimethylsiloxane (PDMS) selective membranes with the addition of zeolite socony mobil – 5 (ZSM – 5), octanitropheyl (ONPS) and octaaminophenyl (OAPS) at various concentration (5 – 20 wt%) were prepared. The result showed that membrane prepared with OAPS showed the best separation factor compared to membrane incorporated with other fillers. The low polarity of OAPS improved the interaction between the filler and furfural. The increase amount of OAPS filler loading could enrich the separation factor because the extra OAPS not only increased the furfural pathway but also decreased the water diffusion rate. The PDMS membrane with 15 wt% of OAPS could purify furfural from 3 wt% to 20 wt% furfural concentration. The increase of feed temperature would improve the total flux of membrane because the partial vapor pressure was increased. The separation factor was increased at the temperature ranged 30 – 50 °C then dropped at 60°C. While at feed temperature 60°C, the effect of free volume would have more impact over the increased of partial vapor pressure so the separation reduced.

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Chapter 1

Introduction

Nowadays, there is a rapidly increasing demand for energy consumption over a limited fossil – fuel resource. Conversely, the resources of energy continue to reduce. The development and a search for renewable energy resources are thus of crucial importance for curtaining a sustained energy management. Biomass is becoming the main developed target for replacing the fossil – petroleum based reserves. Among the various chemical derives from biomass, furfural or 2-furaldehyde is known as a very important renewable, non – petroleum based chemical feedstock and solvent. It can be used in many applications such as a solvent in oils and lubricants or as a reactant for many types of chemicals [1]. However, with a state-of-the-art technology, there still no synthesis reaction to achieve high purified furfural. The recent, furfural synthesis route can only provide furfural concentration at around 3 – 6 wt.% [1]. The only way to gain furfural is lignocellulose biomass dehydrating reaction in which suitable separation method is required to obtain high concentration solution [2].

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Distillation and extraction are normally applied to separate furfural from solution. The distillation is a traditional method, in which water content is evaporated out leaving the more concentrate furfural solution. Through a high concentration of furfural could be obtained, it requires very large energy consumption. The liquid – liquid extraction (LLE) uses a solvent to remove furfural from the feed mixture. The high furfural solubility solvent is filled and dissolves furfural. The obtained furfural extracted solution is then further separated and high concentration furfural could be acquired. However, LLE method demands high amount of chemical solvent that requires the solvent recovery or treatment unit to treat the residuals, leading to an increase in operating cost [3]. Thus, there is a need for an alternative separation process that is economic and more energy friendly for the furfural recovery. Pervaporation is a well - recognized energy friendly and effective separation tool for recovery of valued (semi) volatile substances at relatively low concentration in feed [2]. If the suitable membranes, the key element, are available, pervaporation could be a promising option and the best alternative to the conventional distillation and LLE.

For the purpose of furfural – water separation via pervaporation, hydrophobic membrane is required for a good membrane performance, which is normally determined by flux and separation factor. Unfortunately, these two factors always show contrary trend called trade – off phenomena. In order to achieve the high - performance membrane, many strategies have been applied. These include the modification of membrane structure, chemical properties, and hydrophilicity. In order to fabricated a suitable pervaporation membrane, polymers that can provide hydrophobic properties were normally used solely or in a combination with other nanostructure fillers that can further improve the mechanical or thermal stability of the membrane [4, 5].

This research aims to develop a new pervaporation membrane by applying a concept of composite materials, combining two distinguish properties of polymer and inorganic fillers. The thesis is divided into six chapters, including introduction, background and literature review, objective and scope of work, experimental, results and discussion, and the conclusion. The introduction part provides the motivation and an overview of the work. The second chapter provides the background and literature reviews of recent development of pervaporation membrane. The third chapter demonstrates the objective and scope of this work. Then in the next section, the chemicals, analytical instruments used in this work and procedure of the experiment are described. The results are then discussed in details. In the final chapter, conclusion and finding from this research are made.

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Chapter 2

Background and Literature review

2.1 Background

2.1.1 Furfural

Furfural (2-furaldehyde) is a liquid chemical known as one of the most remarkable chemical feed stocks from the lignocellulose biomass. Furfural can provide a lot of benefits to many industries by reformed the furfural into new chemical derives such as tetrahydrofuran, furoic acid, furfuryl amine, etc. [6]. With a lot of potential to be used, furfural synthesized reaction and separation method become the target for the research development. Generally, furfural can be produced from the pentosan and water hydrolysis – dehydration reaction with the aid of acid catalyst [7]. In the initial step, the pentosan will hydrolyze with water forming the pentose sugar. Then, the temperature will be risen around 150 °C which resulted in the dehydration of pentose sugar to form furfural and water.

$$Pentosan + Water \rightarrow Pentose$$
$$(C_5H_8O_4)n + nH_2O \rightarrow nC_5H_{10}O_5$$

Sulfuric acid catalyst

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$$Pentose \rightarrow Furfural + Water$$
$$C_5H_{10}O_5 \rightarrow C_5H_4O_2 + H_2O$$

150 °C

The concentration of furfural achieved from the synthesized reaction is around 3 – 6 wt%. Thus, to get the high concentration of furfural, the separation unit are required to purify the obtained solution. There are three separating process to separate furfural and water composed of distillation, liquid – liquid extraction and membrane pervaporation. The distillation method can separate furfural and water at 35wt.% concentration before reach the azeotrope while the liquid – liquid extraction technique can separate the solution up to 70 – 80 wt.% depend on the extract solvent.

The membrane pervaporation shows the best separation performance by can enhanced the furfural concentration up to 95wt.% by using polyureathaneurea membrane [8].

The properties of furfural was also demonstrated in the Table 2.1.

Table 2.1 Properties of furfural [9].

Molecular weight	96.08
Boiling point at 101.3 kPa (1atm) ,°C	161.7
Freezing point , °C	-36.5
Refractive index 25°C , n_D	1.5235
Density at 20°C , g/cm^3	1.1598
Vapor density (air=1)	3.3
Critical pressure P_c , MPa	5.502
Critical temperature T_c , °C	397
Solubility in water , wt.%	8.3
Viscosity at 25°C , mPa.s	1.49
Surface tension , mN/m	40.7
Dielectric constant at 20°C	41.9
Explosion limits (in air), vol%	2.1 – 19.3
Flash point , °C	61.7
Auto ignition temperature , °C	315

2.1.2 Membrane preparation

There are many techniques for preparing membranes. However, immersion precipitation - phase inversion is one of the most remarkable and simple techniques to fabricate the membrane. Based on its definition, the phase inversion is a procedure, in which a polymer is transformed from liquid phase into solid phase in a control manner [10]. In the preparation procedure, polymer will be dissolved with a solvent to obtain polymer solution and cast on a support. The cast polymer is then immersed with a non – solvent solution in a coagulation bath, which mostly is water. The mass transfer between solvent and non – solvent leads to the precipitation of membrane gel. In many cases, an additional dense thin film is coated on top of prepared membrane and works as the selective layer. The membrane, composing of two layers from different materials, is called composite membranes. In general, the top surface is the selective layer, which is mostly dense while the lower layer works as the support. The support layer is generally more porous to facilitate the permeation flux. This supporting layer is normally cast on a non – woven backing fabric to further provide the mechanical strength and the durability of the membrane. In the phase inversion, many parameters can influence the final membrane structure such as polymer types, polymer concentration and solvent non – solvent pairs. Type of polymer can also affect hydrophilicity, thermal and chemical stability of the membrane. While, polymer concentration affects structure and porosity of the membrane; higher polymer concentration will generally lead to higher polymer precipitation at the interface, resulting in lower porosity of membrane. Furthermore, the addition of nanoparticle can also influence membrane structure and properties by changing their mixture phase system [11].

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2.1.3 Pervaporation process

Membrane pervaporation is a relatively new membrane technology under a developing state for industrial application. Membrane pervaporation is used for separating components in a liquid mixture by partly vaporizing the target component and selectively transferring the vaporized target molecule through a semi-permeable membrane. The principle of membrane pervaporation is depicted in Fig. 2.1, using furfural removal as an example. With the aiding of the reduction of pressure in permeate side, meaning that the boiling point of the solution at permeate side will be reduce. This helps stimulating the evaporation of the mixture. The solution that can pass through the membrane (permeate) is condensed and collected, whereas the feeding mixture that cannot pass through membrane (retentate) will be circulated to the feed tank. The mass transfer involved in the pervaporation process comprises of three steps;

1) The sorption of the feed mixture into membrane at surface layer,
2) The diffusion of the components in the surface layer through the membrane, and
3) The desorption of components to permeate side.

In the sorption step, the ability of components to get sorption to the membrane depends on an interaction force between solution and membrane. For example, hydrophobic membrane can interact with non – polar component better than the polar component. Second, the diffusion of permeated molecules depends on size, molecular weight, membrane structure, and thickness. Permeate molecules with small size and low molecular weight can pass through membrane faster as their diffusivity is normally greater than the large molecule with high molecular weight. In addition thin and porous membrane can enhance the permeate flux due to the short distance (less resistance) that the permeate solution have to travel through [12]. In pervaporation process, there are some challenges that affect the process performance. One of them is the plasticizing effect, in which the solute molecule interacts with polymer and causes the change in membrane structure. Normally, the change of membrane structure will increase the flux because of the enlargement of membrane free volumes; however, it will reduce the membrane separation factor because the undesired molecule will also easily pass through this free volume. Another effect is called the coupling effect that occurs when molecules of the two components interact to each other and form a larger molecular size. This effect will decrease the diffusion rate, but will promote in the high swelling membrane, which creates more free volume in membrane structure [10, 13].

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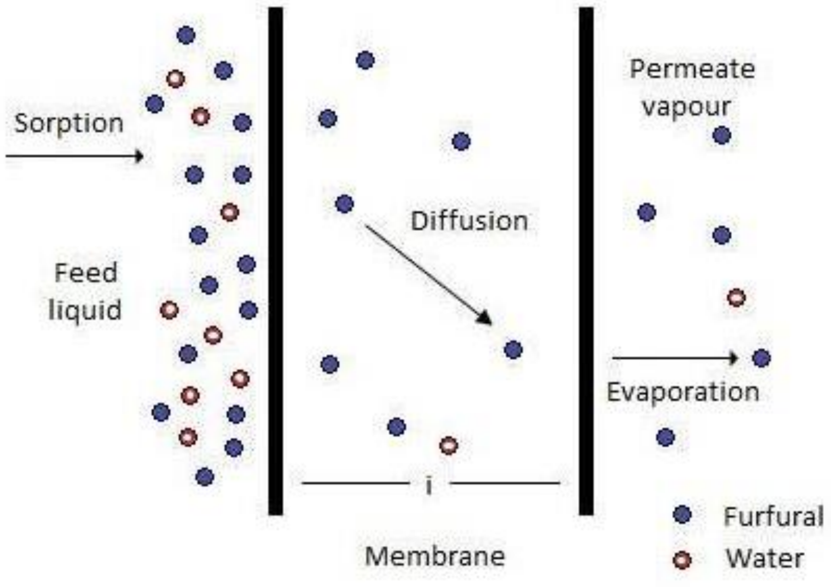

Fig. 2.1 Membrane pervaporation principle.

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Operating parameters in pervaporation process also play an important role to the membrane performance. These parameters include feed concentration, feed temperature, and permeate pressure. When increased feed concentration, the component flux increases due to the increase in component activity and the raise of driving force from the increase of concentration difference between feed and permeate. Generally, the separation factor would decrease due to membrane tend to swell better with the increased feed concentration. This lead to polymer chain mobilizing and create more free volume, so other molecules can pass through membrane easier [2, 8, 14-16]. Increasing temperature will also increase the flux because it is easier to vaporization. The partial pressure of components in feed side will be raised while the permeate pressure still remain unchanged, so the driving force will also be increased. Moreover, the shifting of polymer chain occurs and lead to more free space and the lessening of separation factor [2, 5, 16, 17]. Reduction of permeate partial pressure resulted in the decrease of the boiling point of permeate solution, leading to an easier vaporization. In addition, the reduced permeate pressure will increase the driving force of the system. With these two reasons, the flux is improved [10]. The separation factor and flux can be calculated from the following equations [8, 16].

$$J = \frac{Q}{At} \tag{1}$$

Where J is the flux (g/m^2h), Q is the weight of permeate obtained at time, t, and A is the effective membrane area.

$$\alpha_p = \frac{C_{i2}}{C_{i1}}\frac{C_{j1}}{C_{j2}} \tag{2}$$

$$\alpha_P = \frac{Y(1-X)}{X(1-Y)} \tag{3}$$

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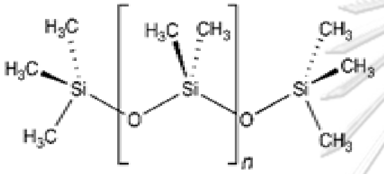
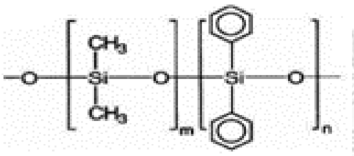
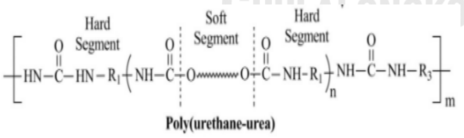
α_p is the separation factor for permeation of the solute. C_{i1} and C_{i2} are the concentration of the solute in feed and permeate, respectively. C_{j1} and C_{j2} are the concentration of solvent (water) in feed and permeate, respectively. X is weight faction of furfural in feed and Y is weight faction of furfural in permeate.

2.2 Literature review

Pervaporation membrane for separating organic – water solution has been well developed; however, there are still a limited number of research studies, reporting the furfural recovery. Polymers frequency used for making pervaporation membranes for furfural recovery include polydimethylsiloxane (PDMS), polybutadiene based polyurethaneurea (HTPB – PUU), and polymethylphenylsiloxane (PMPS). The chemical structure and property of these polymeric membranes are compared in Table 2.2.

Table 2.2 Properties of polymeric membranes used in furfural separation.

Name and chemical structure	T_g (°C)	Mechanical strength (shear elastic modulus)	Total flux $gm^{-2}h^{-1}$	Separation factor
PDMS 	-125	250 kPa [18]	1,600	35
PMPS 	-36	200 – 400 kPa [19]	900	53.3
PUU 	-40	200 – 800 kPa [20]	44	340

* Compared at operating temperature at 60-80 °C, and feed concentration at 1-2 wt.% furfural

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Polydimethlysiloxane (PDMS) is one of the most widely used membranes for separating organic – organic liquid mixtures and removing volatile organic compounds from water and soils [17]. The PDMS membranes were used for separating furfural aqueous solution. The results showed very high furfural flux up to 300 – 4,000 $gm^{-2}h^{-1}$ with the separation factor at around 20 – 80 which is considered moderated when compared to other polymers. The very high flux and moderated separation factor might be because the high porous structure and very thin selective layer of PDMS membrane [1, 2].

Polymethlyphenylsiloxane (PMPS) is another polymer membrane used for separating furfural and water. PMPS is a polymer membrane in a sub – family of the polysiloxane with methyl group substituted by phenyl. The researchers believed that the substitution of phenyl group can enhance the selectivity of the membrane [21]. There was an investigation, using the PMPS membrane in the furfural separation. The result showed the moderate flux which is lower than PDMS but higher than PUU. While, the separation is higher than PDMS but lower than PUU [4].

The last one is polybutadiene based polyurethaneurea (HTPB – PUU). It has a specific polymer chain structure and morphology, comprising of a flexible soft segment (selective part) and a rigid hard segment (supporting part). The experiment found that the HTPB - PUU can separate furfural with high separation factor, but very low flux. This low flux might be because of the structure of the prepared membrane that appeared to be very thick and dense. Furthermore, the superhydrophobic nature of HTPB also help raising the separation factor [8, 14].

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Desired membranes used for separation technology should has high separation and flux. But, in fact, these two factors always show a contradict trend. When one factor is high, the other is usually poor. Thus, it is necessary to find the optimal and suitable point for these two parameters. In general, the improvement of membrane performance can be divided into two simple ways to either 1) increase the total flux or to 2) increase the separation factor. Many recent research studied based on the above mentioned purposes are summarized in Table 2.3.

Table 2.3 The current research studied on membrane development for furfural

Membrane – solution to separate	Filler or variant	Filler loading	Feed conc. (wt.%)	Temp. (°C)	Separation factor	Total flux ($gm^{-2}h^{-1}$)	Permeate conc. (wt.%)	Ref.
PDMS/PVDF - water/furfural	DBSA	-	0.5	35	82.3	235.7	27.52	[1]
			3.5		45.5	1297.5	62.27	
			6.5		24.1	5123.4	62.62	
	SDS	-	0.5		82.0	243.5	29.18	
			3.5		46.9	1283.2	62.98	
			6.5		23.8	5162.7	62.33	
			0.5	80	53.7	1050.7	21.3	
			3.5		34.5	1922.4	55.6	
			6.5		27.6	4049.3	65.8	
			6.5	95	23.9	5162.7	62.4	
PDMS/PVDF - water/furfural	DBSA	-	1	35	48.5	300	33.5	[2]
				80	35	1600	27.5	
				95	28.5	2300	23	
			3.3	35	46	600	62	
				80	31.5	2500	53	
				95	25	3200	45	
			6	35	38.5	1000	72	
				80	27.5	2900	64	
				95	21	4250	59	
Silicon rubber (PDMS) - Phenol/furfural/Guaicol	-	-	0.02	40	62	- (no specify)	1.23	[22]
				80	56		1.11	
				100	38		0.75	
				120	30.2	4.33	0.6	
PMPS - water/furfural	HOSSM-ZIF7	41.3 wt.%	1	80	35.9	670	26.1	[4]
	HOSSM-ZIF8	41.3	1	80	53.3	900	35.00	

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Membrane – solution to separate	Filler or variant	Filler loading	Feed conc. (wt.%)	Temp. (°C)	Separation factor	Total flux ($gm^{-2}h^{-1}$)	Permeate conc. (wt.%)	Ref.
				100	42.9	1400	30.23	
				120	17.6	1800	15.09	
HTPB-PUU -Water/furfural	Diamine	20 mole%	2	30	88	12.5	63.5	[8]
				75	340	44	87	
			6	30	56	18	77	
		50	2	30	95	11.5	66	
				75	375	36	88	
		70	2	30	100	10	68	
				75	450	32.5	89	
		100	2	30	113	7.5	69	
				75	640	27.5	95	
Modified HTPB-PUU - water/furfural 50% diamine	LiCl	0	2	30	88.6	7.2	64.4	[14]
		0.5 wt.%	2	30	85.2	13.6	63.5	
				75	285	46.5	85	
			6	30	55	24.5	77.5	
		1	2	30	80.3	17.0	62.1	
				75	247	47.5	83	
			6	30	48.5	-	74	
		2	2	30	74.4	19.6	60.3	
Chitosan/POSS -Water/ethanol	-	-	10	30	60	51	62.5	[5]
	Octaanion (OA)	1	10	30	240	34	96.39	
		5			300	28	97.09	
		9			110	41	92.44	
	Octanitrophenyl (ONPS)	1	10	30	220	22	96.07	
		5			130	42	93.53	
		9			105	55	92.11	
	Octaamino-phenyl (OAPS)	1	10	30	230	40	96.23	
		5			375	30	97.66	
		9			305	32	97.13	
	Octaammo-nium (OAS)	1	10	30	200	42	95.69	
		5			205	38	95.79	
		9			195	38.5	95.59	

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Membrane – solution to separate	Filler or variant	Filler loading	Feed conc. (wt.%)	Temp. (°C)	Separation factor	Total flux ($gm^{-2}h^{-1}$)	Permeate conc. (wt.%)	Ref.
Pebax/POSS -Ethanol/water	Octa (3-hydroxy-3-methylbutlydimethylsili-xy(AL0136)	1	5	25	4	115	17.39	[23]
		5			4.2	145	18.10	
		10			4	105	17.39	
	Disilanoliso-butyl (SO1440)	1	5	25	3.5	100	15.56	
		5			3.9	82	17.03	
		10			2.6	60	12.04	
PDMS -Ethanol/Water	**ZSM – 5**	**0**	**10**	**60**	8.1	**680**	47.37	[21]
		10			9.5	**780**	51.35	
		20			10.8	**990**	54.54	
		30			13.5	**1200**	60	
		40			10.2	**1350**	53.12	
PDMS -Ethanol/water	**ZSM - 5**	**0**	5	40	7.8	**2300**	29.1	[22]
		10			8.1	**2200**	29.89	
		20			8.4	**1300**	30.65	
		30			10.9	**750**	36.45	

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The simplest and most straight forward strategy to increase the total flux of permeates is lowering membrane resistances by increasing membrane porosity and reducing membrane thickness. Several pore forming additives, such as dodecylbenzenesulphonic acid (DBSA), sodium dodecyl sulfate (SDS), diamine, and LiCl, were used to control porosity of the membrane during membrane fabrication step. This attempt was mainly to reduce mass transfer resistance of the membranes. For instance, Ghosh et al., investigated the furfural pervaporative separation using modified HTPB – PUU membrane [14]. Due to very low total flux of PUU membrane, they attempted to increase the porosity of membrane by adding lithium chloride

(LiCl) in the polymer mixtures and leaching it out during membrane formation via the phase inversion. The result demonstrated that this strategy can enhance the total flux. Sagehashi et al., studied the separation of phenols and furfural by pervaporation and reverse osmosis membrane [22]. They varied membrane thickness and found that the reduction of membrane thickness could increase total flux of the membrane.

The improvement of separation factor for polymeric membrane has also been tried out. Ghosh et al. examined the ratio between soft block content and hard segment in HTPB - PUU membrane structure by varied the concentration of diamine in polymer mixtures [8]. They found that the excess of hard block content can improve the separation factor because it promoted low free volume and dense structure.

Recently, the concept of composite materials by an addition of nanofillers in polymer matrix has gained tremendous attention and was applied in the development of many novel pervaporation membranes. Various filler types such as zeolite, zeolitic imidazolate framework (ZIF), and polyhedral silsesquioxane (POSS) were applied to form a composite membrane combining advantages of two different materials. The fillers that could well incorporated with the polymer include the ability to improve the separation factor (selective to permeate) or the total flux (porous structure) were the targets to study.

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Zeolite is microporous aluminosilicate crystalline, which composed of Al, Si and O (SiO_4 or AlO_4) bonded into the tetrahedron shape. The property such as good adsorption, porous structure, accommodate to the dipole and molecular sieve made zeolite become the popular filler many materials [24]. The ratio of Si and Al or the structure of filler could influence their property. Zeolite socony mobil – 5 (ZSM – 5) is a type of zeolite having several pentasil units linked together by oxygen bridges to form a pentasil chain. A pentasil unit consists of eight five member rings which were Al, Si or O. Liu et al., [25] mixed ZSM – 5 in PDMS membrane to form a composite membrane for separating ethanol and water. The total flux and separation factor of membranes were improved due to the selectivity of ethanol through ZSM – 5 and the compatibility of hydrophobic ZSM - 5 in PDMS polymer. Liu et al., [26] also prepared the ZSM – 5 PDMS/ceramic membrane to separate ethanol and water. Similar trend of improved separating performance was reported.

Zeolitic imidazolate framework (ZIF) is the subset of metal - organic framework (MOF). MOF is the compound comprising of the metal ions coordinate to the organic ligands forms into the network structure. While the ligands of MOF could be any atoms or molecule, the ligands of ZIFs was restricted to be imidazolate rings. Many research reported that ZIFs had many great properties such as superhydrophobicity, robustness, high porosity, and thermal and chemical resistance [4]. ZIF – 8 is one type of the ZIFs with the cubic soladite structure having Zn coordinated with four imidazolate rings. Liu et al. incorporated ZIF – 8 in PMPS [4]. The result showed that the addition of ZIF – 8 fillers enhanced furfural - water separation factor and the flux. This was because ZIF – 8 exhibits superhydrophobic and has exceptional adsorption selectivity toward least polar organic molecules like furfural.

Polyhedral oligomeric silesquioxane (POSS) is the organosilicon compound having chemical formula $(RSiO_{1.5})_n$ with the Si – O bond in a cage – like shape. POSS showed the potential to improve to the thermal and chemical stability, compatible to the polymer and oxidation resistance [27]. The functional group and the amount of Si have a strong impact on the property of POSS. At low numbers of Si, POSS is in the white solid phase while at higher Si amount, it becomes more fluidity. Xu et al., have investigated the effects of POSS on performance of the chitosan hybrid membranes [5]. The addition of POSS nanoparticles improved the separation factor of the membrane while slightly reduced total flux. POSS was also applied into the poly – ether – amide (PEBAX) to separate water and ethanol [23]. It was found that the addition of POSS improved both total flux and separation factor of membranes owing to the affinity toward ethanol of POSS.

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For a better visualization of the performance of membranes prepared from different strategies, as mentioned before, their flux and separation factor (from Table 2.3) are plotted in Fig. 2.2.

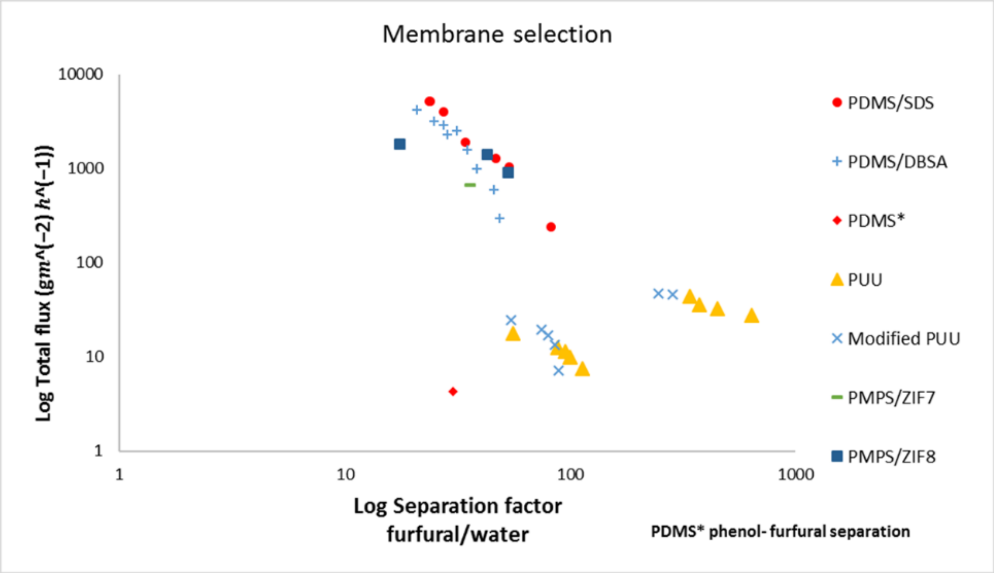

Fig. 2.2 Comparison of flux and separation factor of various membrane materials

From the literature, it would be concluded that PDMS based membrane could provide high permeate flux, however its ability to separate furfural from water was fairly low compared to other polymers. There were many research studies, incorporating additive to the PDMS just to further improve its flux. However, there is only few research study attempting to improve its selectivity. Thus, this research aimed to improve selectivity of PDMS while maintaining its high flux by applying the concept of composite materials combining selective properties from the additional material. Nanofiller such as ZSM – 5 and POSS was used as the additive.

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Chapter 3

Objective and Scopes of work

3.1 Objective

1. To investigate the effect of type and loading of fillers on membrane structure, hydrophilicity and performance in furfural recovery by pervaporation.
2. To study the effect of operating temperature on membrane separation performance in pervaporation process.

3.2 Scopes of work

3.2.1 Membrane fabrication

Membranes were fabricated via a phase inversion technique based on a polyvinylidene fluoride (PVDF) support with non – woven backing fabric. The selective layer was made of polydimethylsiloxane (PDMS) and was coated on the PVDF support layer by a dip coating method. The effects of the following parameters related to the selective layer (PDMS) will be investigated.

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- Filler type: ZSM - 5 and POSS (octanitrophenyl and octaaminophenyl)
- Filler loading: 0 - 20 wt.%

3.2.2 Pervaporation performance

The performance of the prepared membranes will be evaluated and compared. The following operating conditions will be controlled during the pervaporation process.

- Feed concentration of furfural in water: 3 wt.%
- Feed temperature: 30 – 60 ˚C
- Feed flow rate: 200 mL/min
- Vacuum pressure: 100 mbar

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Chapter 4

EXPERIMENTAL

This chapter describes research methodology applied to this work. The first part explains the chemicals and materials used. Second, the method of membrane fabrication is clarified. Next, the characterization is showed. Last section is the membrane performance test in pervaporation method.

4.1 Chemicals and materials

Polyvinylidene fluoride (PVDF, M_w ~ 275,000) was purchased from Sigma – Aldrich. The novatexx 2470 nonwoven fiber (Viledon – Freudenberg) was used as a backing support.Commercial PDMS membrane was purchased from PERVATECH. Polydimethylsiloxane hydroxyl terminated (PDMS, viscosity ~ 18,000 – 22,000 cSt) and N,N – Dimethylformamide (DMF, AR grade QReC) were supplied from Sigma – Aldrich, respectively. Tetrahydrofuran (THF, 99.5%), Dibutyltin dilaurate (DBTDL, 95%) and Tetraethyl orthosilicate (TEOS, 99%) were purchased from Sigma - Aldrich. Furfural (M_w ~96.08, 99% purity) was purchased from Sigma – Aldrich. Zeolite socony mobil 5 (ZSM-5, CBV 8014 Si/Al = 40) was purchased from Zeolyst. Polyhedral oligosilsesquioxane (POSS) type octanitrophenyl (ONPS, M_w ~ 1,393 g/mol.) and octaaminophenyl (OAPS, M_w ~ 1,153 g/mol.) were purchased from Mayaterials. All materials were used as received except ZSM-5 that was calcined at 300 °C for 30 minutes before use.

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4.2 Membrane preparation method

PVDF support layer was obtained via a phase inversion technique. 24 wt.% of PVDF was dissolved in DMF under a stirring condition. When the uniform homogeneous solution was achieved, the prepared solution was cooled down at room temperation. The prepared polymer solution was cast on a nonwoven backing support (NOVATEXX, 110 μm thickness) with a controlled casting thickness of 0.25 mm. The cast film was immediately immersed in a water bath. The obtained PVDF support membrane was then dried at 50 °C in an oven overnight and kept in a Zip-lock bag until being used.

The selective PDMS layer was coated on top of the prepared PVDF support via a dip coating method. Specifically, PDMS solution was first prepared by mixing 22.32 g of PDMS polymer with 100 g of THF with a stirring condition at room temperature. The polymer solution was then mixed with 2.23 g of TEOS and 0.45 g of DBTDL. After the solution was stirred at room temperature for 1 hours, it was coated on PVDF support membrane using auto dipping applicator with up speed at 100 mm/min, down speed at 200 mm/minute and dwell time at 30 sec. Subsequently, the membrane was dried in an oven at 60 °C for 24 hrs.

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For the preparation of composite membrane, ZSM – 5 and POSS was incorporated in the selective layer of PDMS by mixing the desired amount (5 - 20 wt.%) of the fillers in PDMS solution and stirred until homogenously mixing. Then the same amount of TEOS, DBTDL was added. The other steps during the preparation of the composite membrane were kept the same as of the plain membrane.

4.3 Characterization

4.3.1 Characterization of the organic fillers

- **Particle size**

  The particle size of nanofillers (ZSM – 5 and POSS) is examined by using a scanning electron microscope (SEM, Hitachi S-3400N).

4.3.2 Membrane characterization

- **Thickness**

  Membrane thickness is measured by a digital caliper (TLEAD, 101-2601).

- **Morphology**

  The morphology and structure of prepared membranes were investigated by scanning electron microscopy (SEM, Hitachi S-3400N). The samples were fractured in liquid nitrogen and coated with gold spattering for 60 secs.

- **Chemical structure**

  The infrared spectra of membranes were gained from attenuated total reflectance (ATR) - fourier transform infrared spectroscopy (FTIR) (Nicolet 6700). Each membrane samples were measured at five random spots.

- **Hydrophilicity**

  The hydrophobicity of membranes was measured from contact angle goniometer (OCA – 40, DataPhysics) using water 1 µl per drop. All membranes were also measured for five points and the averaged value was reported.

4.4 Membrane performance test in pervaporation process

Membrane performance of furfural – water separation was evaluated by pervaporation method. Separation factor and total flux of membrane were determined as the membrane performance. All membranes were tested at 30, 40, 50 and 60 °C with a controlled furfural feed concentration at 3 wt.%.

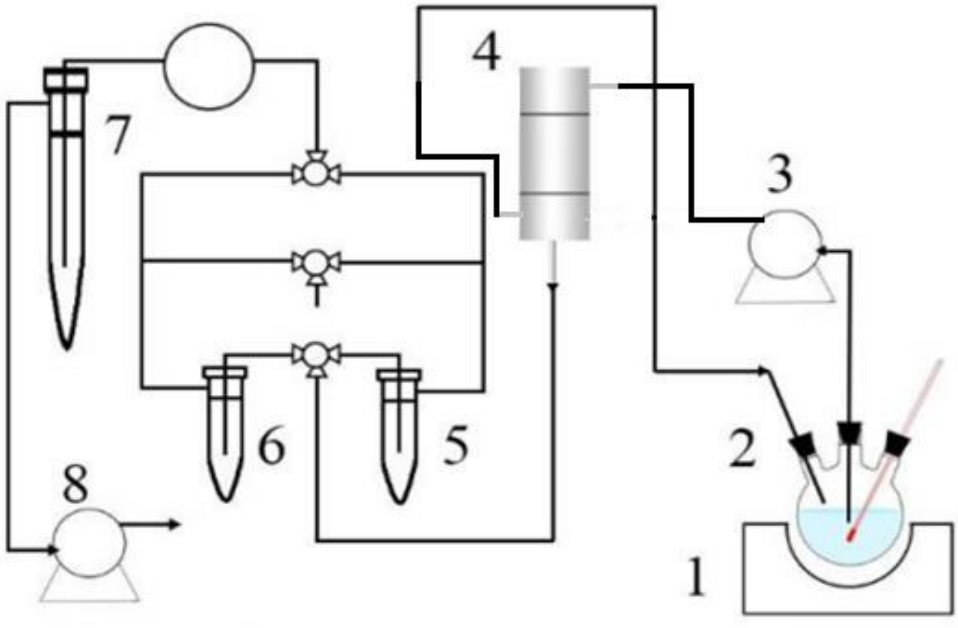

Fig. 4.1 The scheme of pervaporation process 1) magnetic stirrer and heater bath 2) feed reservoir 3) feed peristaltic pump 4) membrane module (5 - 7) cold traps 8) vacuum pump [29].

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The lab-scale pervaporation process is demonstrated in Fig.4.1. The effective area of membrane was 15.21 cm^2 (3.9 centimeter width and 3.9 centimeter length). The applied feed mixture was furfural – water solution with a desired concentration. The feed flow rate was keep constant at 200 mL/min and the stirred speed was set at 150 rpm. Feeding solution was keep at 2 L in the Duran glass bottle. The temperature of feed solution was controlled by temperature control system. The pressure in permeate side was maintained below 100 mbar by a vacuum pump. After the experiment, the permeate vapor was subsequently condensed in cold trap by liquid nitrogen and weighed every 1 hour. The concentration of feed mixtures and permeate solutions were analyzed by High-performance liquid chromatography (HPLC, with UV and RID detector, Shimadzu). The permeation flux was measured by weighing the condensed permeate.

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Chapter 5

Results and discussion

5.1 Tuning operating condition

In membrane separation process, it is well acknowledged that feed flowrate has an influence on the membrane performance [2]. Khatinzadech et al. [30] had studied the effect of feed flowrate on separation performance of pervaporation membrane. They found that the increment of feed flowrate could reduce the effect of concentration polarization and improve membrane performance. With increasing flowrate, the feed solution became more homogeneous. Subsequently, the thickness of boundary layer was decreased, resulting in suppressed mass transfer resistance and enhanced total flux. Likewise, the separation factor would slightly be improved from the reduction of concentration polarization. To find the suitable operating condition for our lab-scale setup, effect of feed flowrate (160 – 240 mL/min) on separation performance of membranes was examined. The PDMS commercial membrane was used to test with feed solution containing 3 wt% furfural. The feed temperature and permeate pressure were fixed at 40 °C and 100 mbar, respectively. Total flux and the separation factor as pervaporation performance were evaluated and demonstrated in Fig. 5.1 to 5.3.

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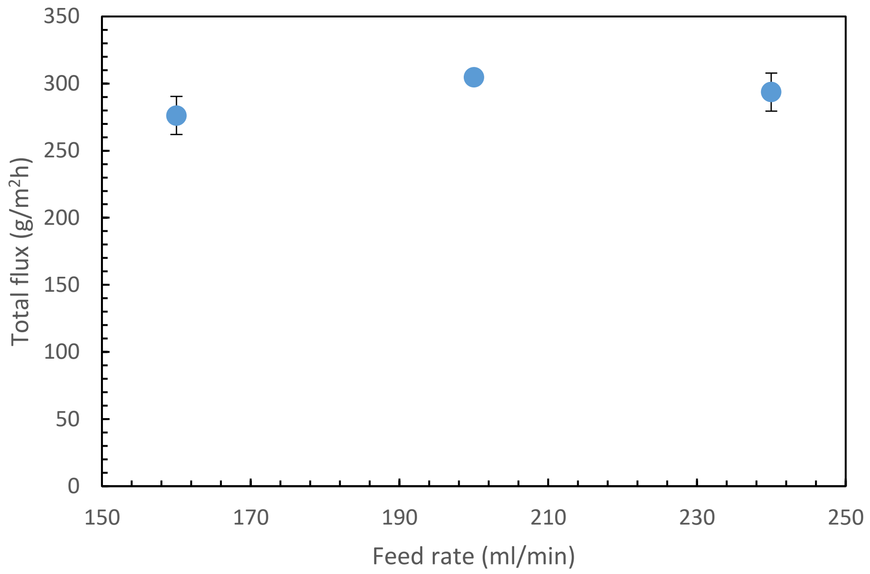

Fig. 5.1 The effect of feed rate on the total flux of commercial membrane tested at 40 °C and 100 mbar.

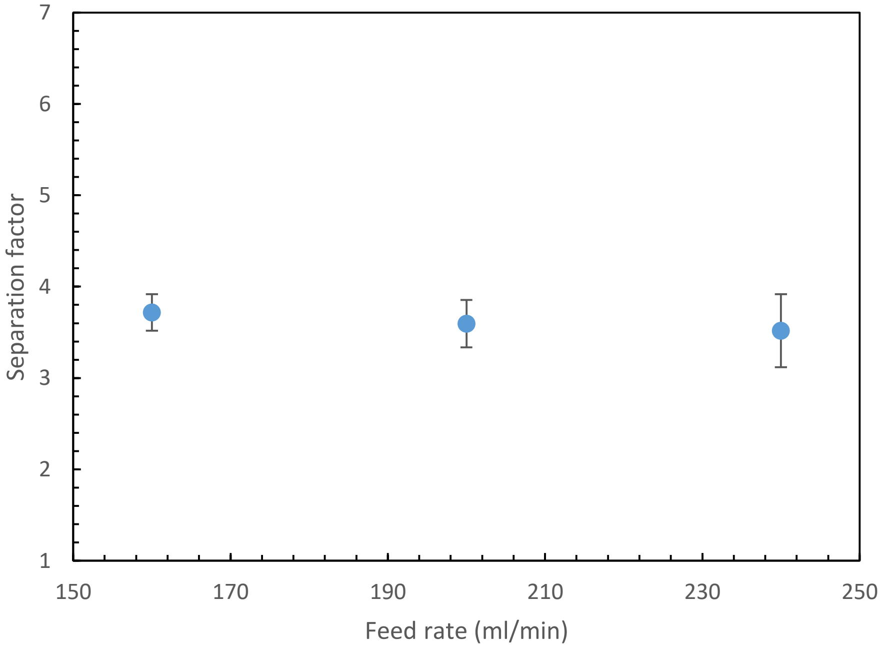

Fig. 5.2 The effect of feed rate on the separation factor of commercial membrane tested at 40 °C and 100 mbar.

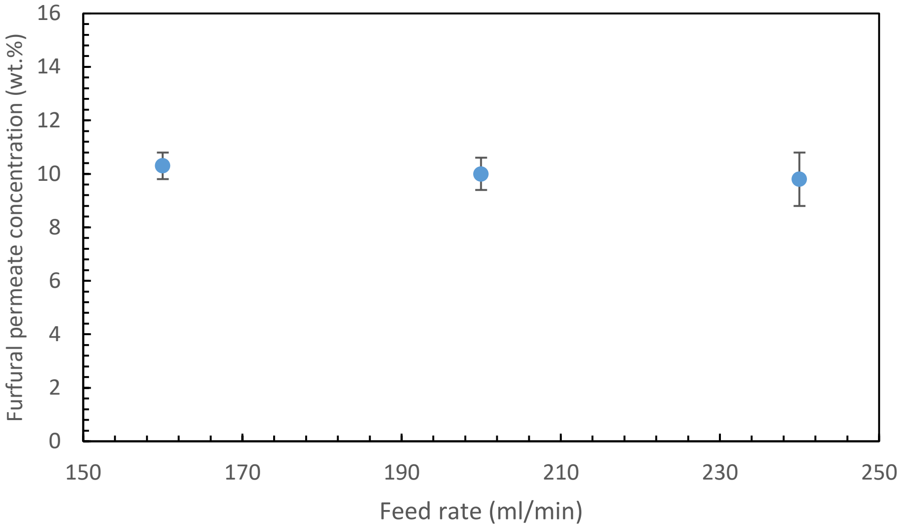

Fig. 5.3 The effect of feed rate on the furfural permeate concentration of commercial membrane tested at 40 °C and 100 mbar.

From Fig. 5.1 to 5.3, the adjusted feed flowrate at 160 – 240 mL/min did not affect the performance of pervaporation membrane. Both total flux and separation factor did not change significantly when the feed flowrate was varied. This might be because of the small effective area of the membrane module used in this research compared to Khatinzadech's report (15.21 cm^2 to 177 cm^2) [30]. In addition, the mixing in small lab-scale process is easily controlled and usually much uniform compared to the bigger one. That made concentration polarization in our work much less pronounced. Therefore, feed flowrate at 200 mL/min was fixed for all following performance tests.

5.2 Screening for a promising filler

This section aimed to screen promising fillers that can further improve the performance of the PDMS. Separation performances (flux and separation factor) combined with filler-polymer compatibility and hydrophobicity were used as the key criteria for the material selection. Three different types of filler (ZSM – 5, OAPS and

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ONPS) were selected to mix with PDMS forming a composite membrane. The properties of fillers such as molecular weight, chemical structure and pore size were summarized in Table 5.1 and their chemical structures were shown in Fig. 5.4.

Table 5.1 Properties of fillers used for this research

Property	Unit	OAPS	ONPS	ZSM – 5
Molecular weight	g/mol	1,153	1,393	4,691
Chemical structure		$(NH_2C_6H_5SiO_{1.5})_8$	$(NO_2C_6H_5SiO_{1.5})_8$	$Na_{2.34}Al_{2.34}Si_{93.66}O_{192}\cdot 16\ H_2O$
Pore size	nm	1 - 3 [27, 31]	1 - 3 [27, 31]	0.54 - 0.55 [32]
Particle size	nm	548 ± 120	508 ± 100	502 ± 170

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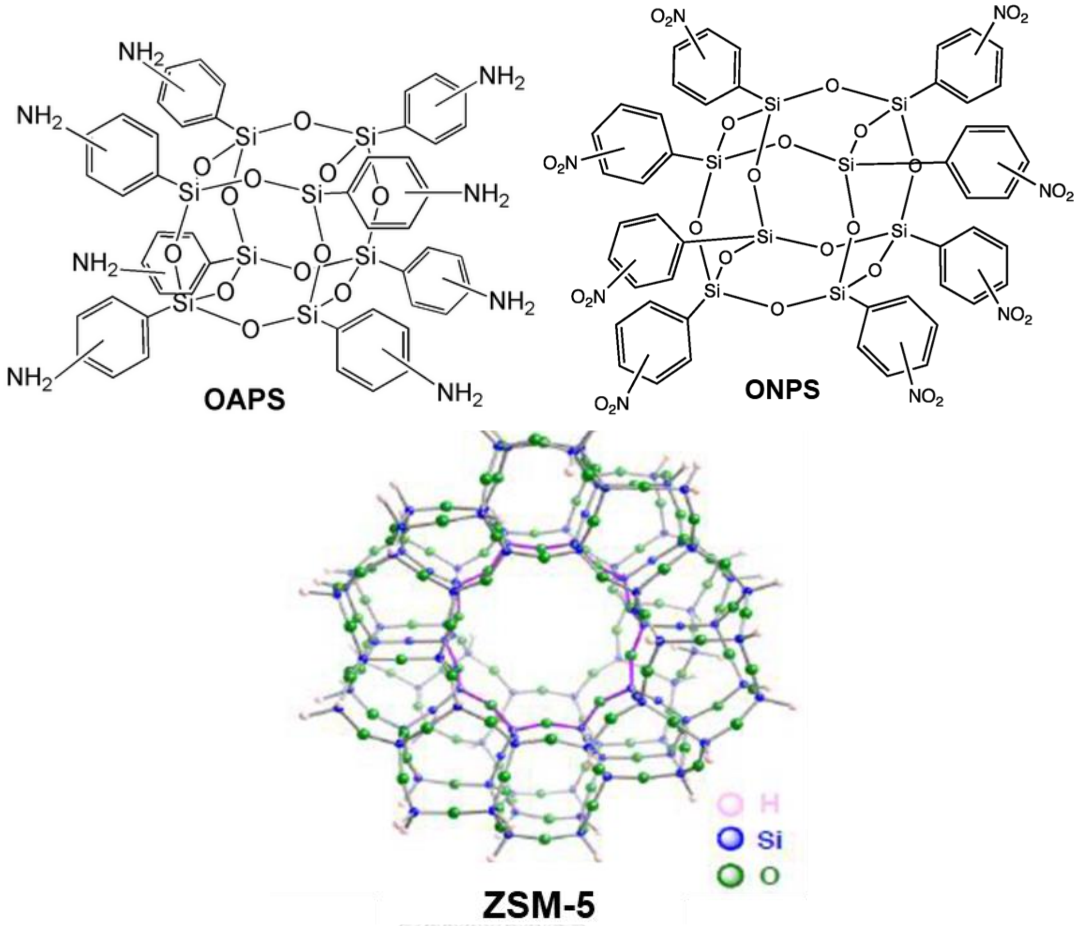

Fig. 5.4 Chemical structure of OAPS, ONPS and ZSM – 5 [33]

ZSM-5 is classified as a zeolite material. It is composed mainly of aluminosilicate minerals. Particle size of ZSM-5 was around 502 ± 170 nm. Whereas, OAPS and ONPS were classified as POSS materials containing silsesquioxane cage structure- like with different reactive functional groups. OAPS had the amine NH_2 as the functional group while ONPS had the nitro NO_2 as the functional group. The particle size of OPAS (548 ± 120 nm) was slightly larger than ONPS (508 ± 100 nm). The pore size of OAPS and ONPS was reported to be around 1 – 3 nm [27, 31] while the pore size of ZSM – 5 was about 0.54 - 0.55 nm [32].

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The amount of filler was fixed at 5 wt% concentration based on polymer weight. Structure, morphology and hydrophobicity of the prepared membrane were characterized. In addition, all prepared membranes were tested in pervaporation process at at 50 °C with feed flowrate at 200 mL/min of aqueous furfural solution at 3 wt% concentration under permeate pressure at 100 mbar. Commercial membrane made of PDMS was also used for a comparison.

Structure, morphology and hydrophobicity of the prepared membranes

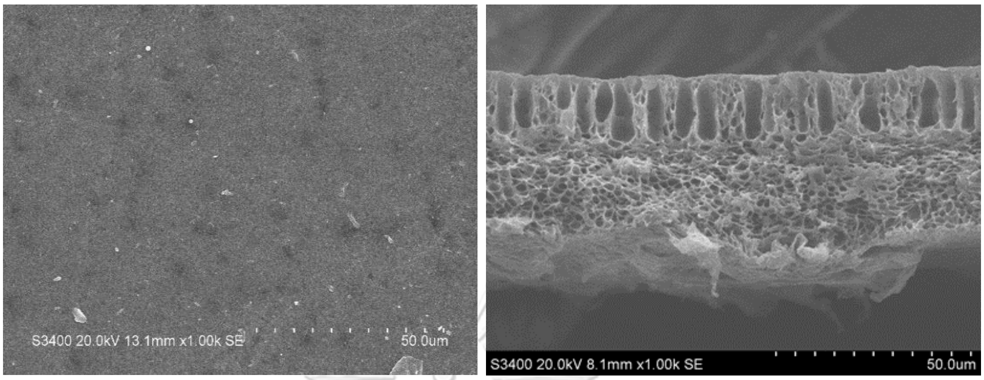
The structure and morphologies of the prepared membranes with different filler types were examined and demonstrated in Fig. 5.5 – 5.8.

From the SEM images in Fig. 5.5, the top surface area of PVDF layer is dense without observable pores. The cross – section image shows that the structure of PVDF layer comprises of two conformations (finger - like and sponge). The finger – like structure is suitable for separation process owing to its vertical shape that will not block the mass transfer of permeate. On the other hand, sponge shape provides more mechanical strength to the membrane.

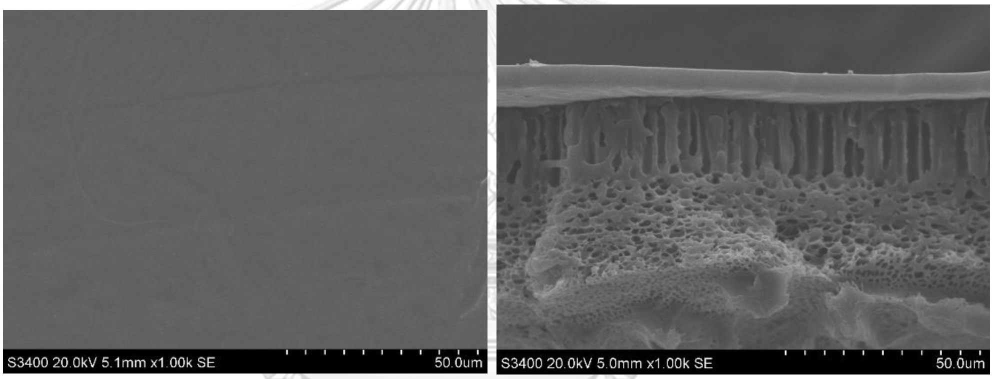
Top surface of PDMS and PVDF membrane show a dense surface. The membrane coated with PDMS layer shows the smoother surface compared to the bare one. Cross section images demonstrate that the top and bottom layers are clearly isolated from each other. Clearly observed from Fig. 5.5, the macropores in sup-layer of the parent membrane did not fulfilled by the PDMS solution after the dip coating. The thickness of pure PVDF support is about 49.76 μm with PDMS layer thickness of 5.48 μm.

The commercial PDMS membrane is composed of two layers. The top surface layer is PDMS selective layer and the bottom supporting layer is polyimide (PI). The top surface of PDMS commercial was dense and no pore was found. The morphology of top PDMS layer was completely compact. In contrast, Polyimide (PI) layer had the long porous finger – like structure. The dense PDMS selective layer thickness was about 4.21 μm while the support PI layer was 30.12 μm.

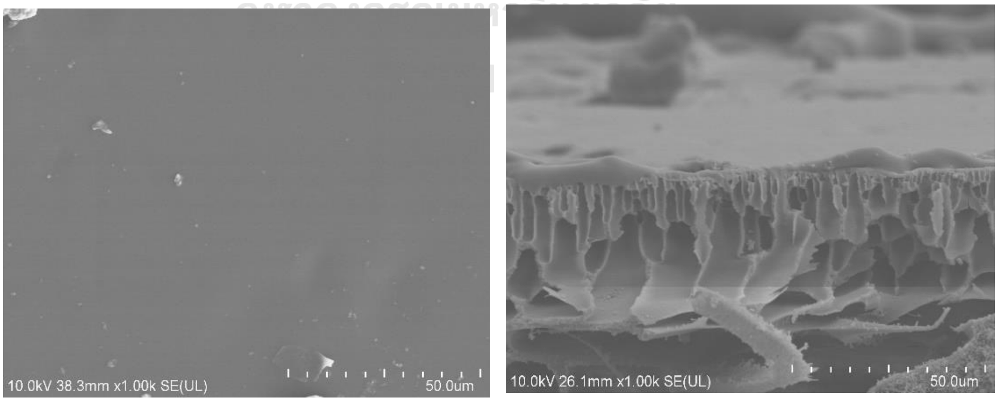
Top surface area Cross – section



PVDF



PDMS



Commercial PDMS

Fig. 5.5 SEM images of top surface and cross - section of PVDF, commercial PDMS and PDMS membranes

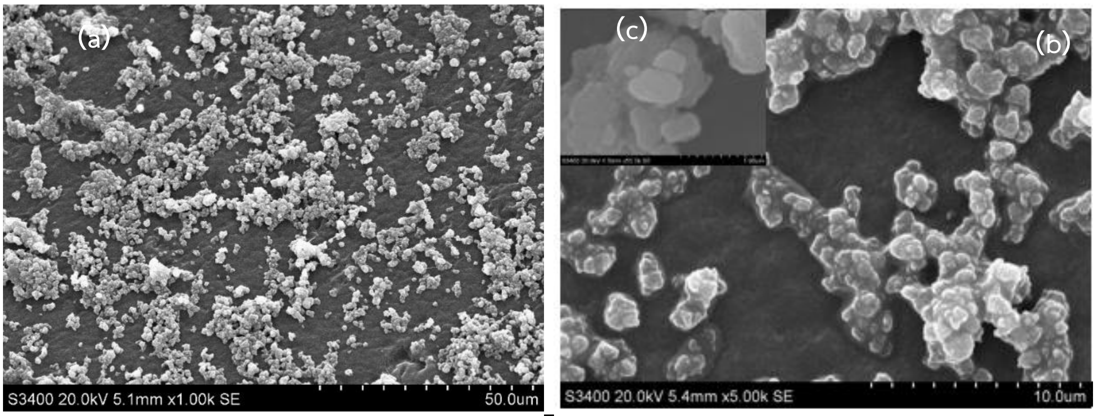


Fig. 5.6 SEM images of (a) top surface of PDMS membrane with 5 wt% ZSM - 5, (b) membrane surface close-up, and (c) ZSM – 5 particle

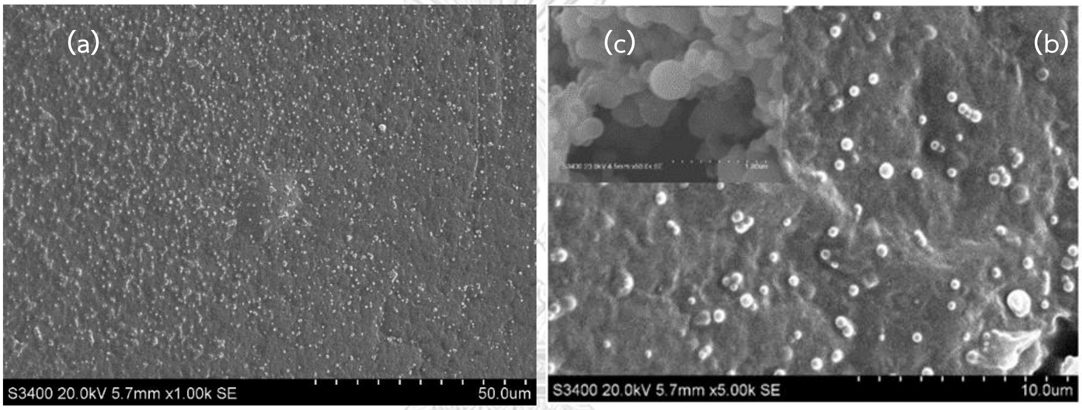


Fig. 5.7 SEM images of (a) top surface of PDMS membrane with 5 wt% ONPS, (b) membrane surface close-up, and (c) ONPS particle

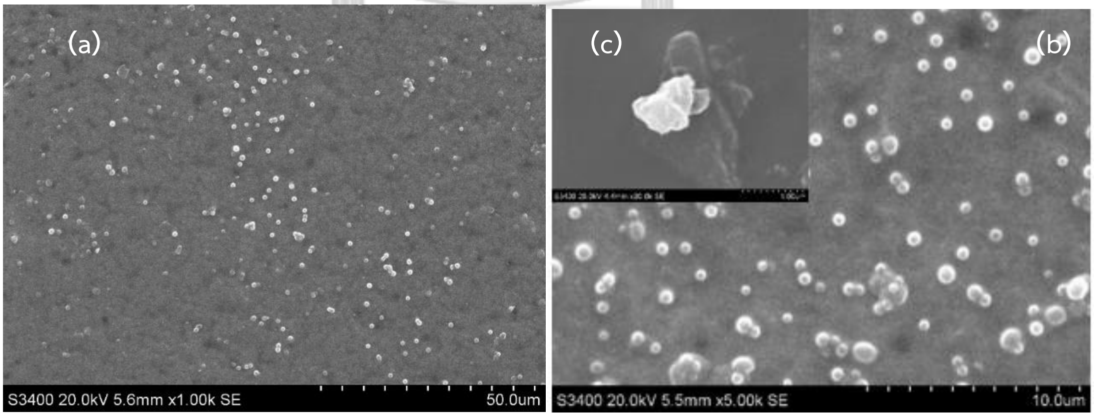


Fig. 5.8 SEM images of (a) top surface of PDMS membrane with 5 wt% OAPS, (b) membrane surface close-up, and (c) OAPS particle

From the SEM images, the addition of ZSM – 5 filler did not incorporate with PDMS polymer and agglomerated on the top surface layer. This was due to the incompatibility between ZSM – 5 and PDMS polymer. PDMS polymer had a high hydrophobic property [1, 2, 17] while ZSM – 5 was quite hydrophilic due to its low Si/Al ratio [32]. Compare to the other researches, the ratio of Si/Al that improved the hydrophobic was about 300 which was almost ten times higher than ZSM – 5 used in this study [25, 26]. On the other hand, OAPS and ONPS with hydrophobic nature was incorporated with PDMS layer and exhibited good dispersion [5]. The similar chemical structure of Si – O in PDMS and POSS (both OAPS and ONPS) could also enhance the compatibility between the filler and the polymer.

The chemical structure of membrane layer is analyzed by ATR – FTIR as showed in Fig. 5.9.

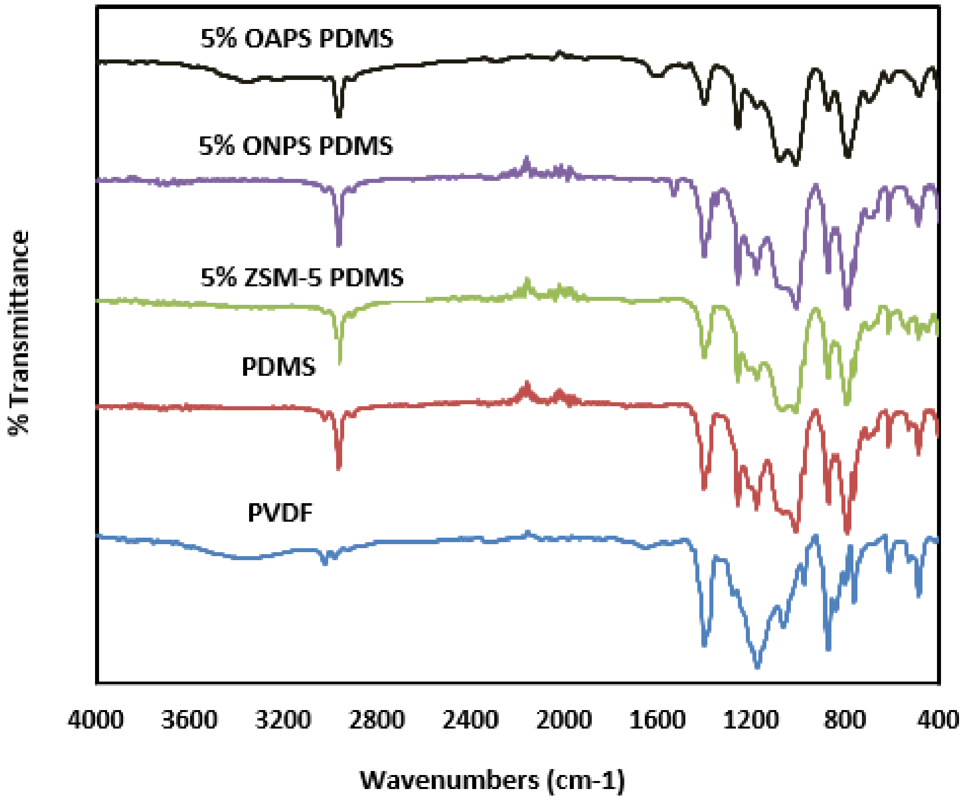


Fig. 5.9 ATR - FTIR spectra of prepared membranes.

PVDF membrane revealed the FTIR spectrum of – CF_2 symmetric stretching vibration at 1,176 cm^{-1}, – CF_2 bonded with – CH_2 at 872 cm^{-1} and – CH_2 bending at

1,443 cm^{-1} [34, 35]. For the bare PDMS membrane, the spectra at 792 and 1,258 cm^{-1} for Si – CH_3, 1,007 cm^{-1} for Si – O bonded and 2,962 cm^{-1} for – CH_3 stretching were obtained. This confirms the succession of coating procedure [36].

For 5% ONPS membrane, the spectra of N – O were found at 1,551 cm^{-1}. The N – O bond was in the functional group of ONPS, so this could verified the existence of ONPS filler in PDMS membrane [37]. The OAPS - PDMS membrane could also be proved by the spectra of N – H at 1607 cm^{-1} and broad peak at 3,363 cm^{-1}[37]. There was no additional peaks from ZSM – 5 membranes compared to PDMS membrane since Al – O bond could not be observed by ATR-FTIR and it was the only bond that is different from those of the bare PDMS membrane.

The hydrophilicity property of membranes incorporated by different filler types was characterized by measuring the water contact angle as represented in Fig. 5.10.

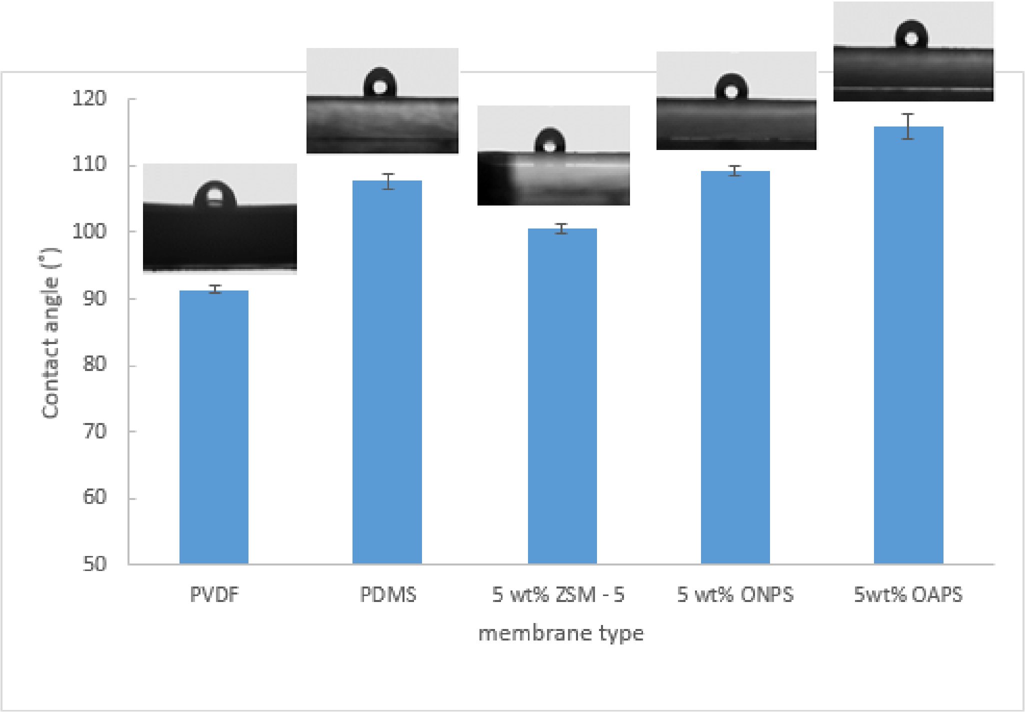


Fig. 5.10 Contact angle of PDMS membranes containing different filler types compared with the bare one and bare PVDF membrane.

From Fig. 5.10, the contact angle of PVDF support layer was about 91.4° showing its hydrophobic property. The contact angle of PVDF support prepared from this work was close to other previous works [38, 39]. Owing to the super hydrophobic nature of PDMS polymer, the PDMS selective layer had the contact angle about 107.7° higher than PVDF supporting layer [1, 17]. This could also confirm the success of dipped PDMS layer on the PVDF.

The addition of ZSM – 5 into the PDMS selective, however, reduced the hydrophobicity of the composite membrane. The electric charge of Al^- and Na^+ caused the ZSM – 5 became more polarity and could interact well with water that promote water transport through the membrane [32]. The incorporated ONPS and OAPS affected the contact angle in the different way. The complete Si – O cage-like structure without any polar of POSS made these fillers naturally hydrophobic. However, different functional groups on POSS contribute hydrophobicity degree differently [31]. This difference could be observed when OAPS and ONPS were mixed with PDMS at the same loading (5 wt.%). The addition of OAPS in membrane resulted in higher contact angle compared to ONPS. This was because OAPS had NH_2 while ONPS had NO_2 as the functional group. The polarity of ONPS was higher than that of OAPS as the NO_2 in functional group had to bond with phenyl group, leading to the dipole of O and N from coordinate covalent bond between them. On the other hand, NH_2 could bond with phenyl group without any emerges of dipole.

<u>Separation performance</u>

The performance of membrane prepared with different filler types was compared and showed in Fig. 5.11 and 5.12.

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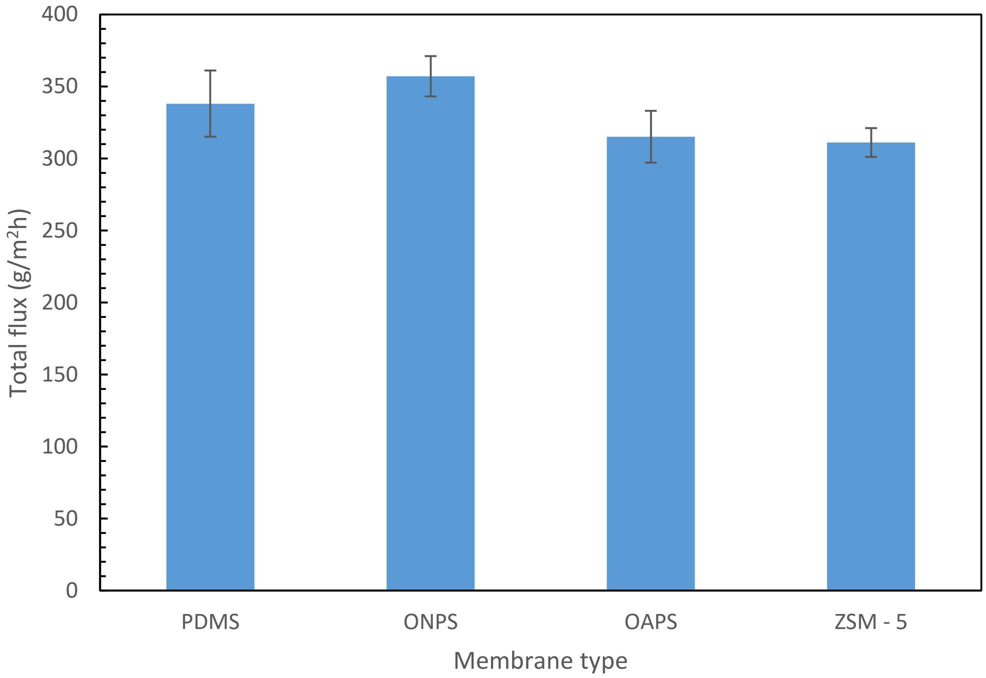

Fig. 5.11 Effect of filler type on the total flux

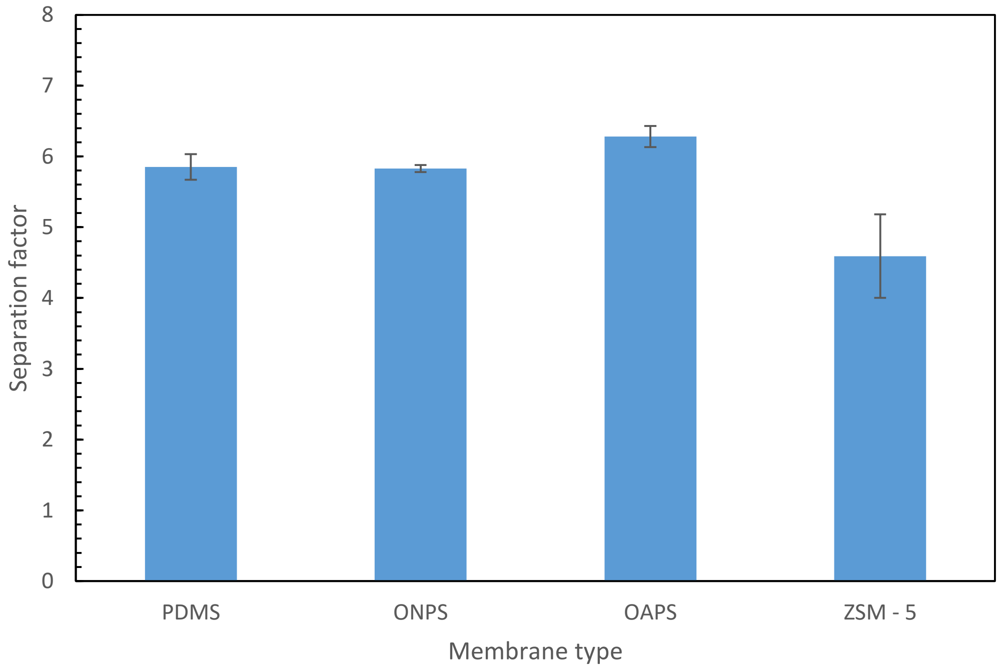

Fig. 5.12 Effect of filler type on the separation factor

The addition of different fillers did not contribute the total flux of membrane but had the impact on the separation factor. Since the separation factor depends on the solubility of solution through the membrane, the contact angle of the membrane would directly affect the separation factor. In this system, water and furfural were two component to be separated. If the contact angle was high, the ability of membrane to absorp the polar molecule will be more difficult. This resulted in decreasing water flux that could get through the membrane.

According to the contact angle result, the addition of ZSM – 5 decreased the contact angle. This resulted in the lower separation factor in the composite membrane with ZSM – 5. As the same reason for OAPS and ONPS, the contact of membrane with ONPS did not change significantly while the contact angle of OAPS increased. Subsequently, the separation factor of membrane with ONPS was around 5.83 close to bare PDMS membrane while the separation of OAPS could be improved.

OAPS was selected as the key filler to study the loading effect as the result showed that it had potential to improve the separation factor of the membrane. The compatibility of OAPS in PDMS resulted in the good dispersion of filler due to their similar hydrophobic Si – O bond structure. The high contact angle of OAPS PDMS membrane and the potential to interact with furfural could enhance the separation performance.

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5.3 Effect of OAPS filler loading on membrane structure and property related to separation performance

The effect of OAPS as the filler was further investigated. The effect of filler loading on membrane structure, morphology and properties was examined.

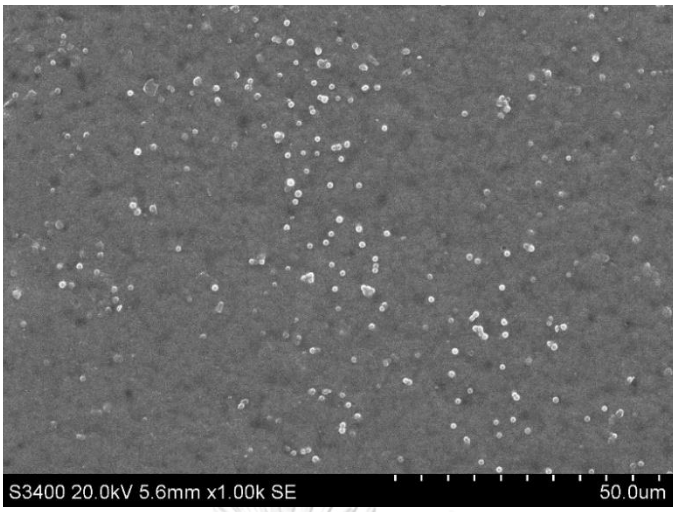

Fig. 5.13 5 wt.% OAPS-PDMS top surface area

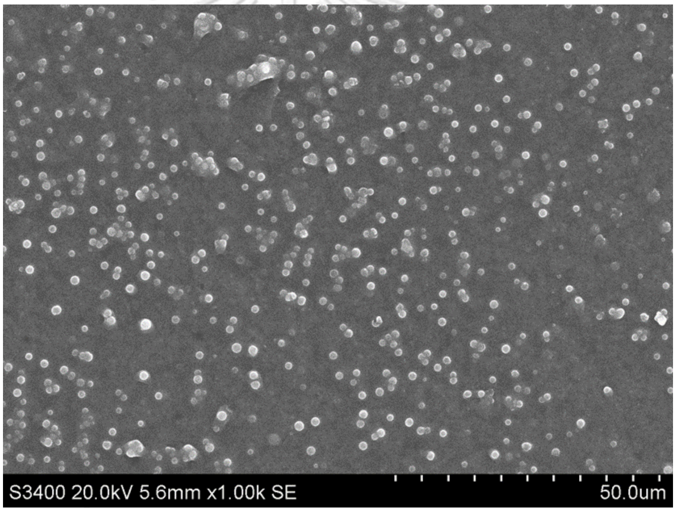

Fig. 5.14 10 wt.% OAPS-PDMS top surface area

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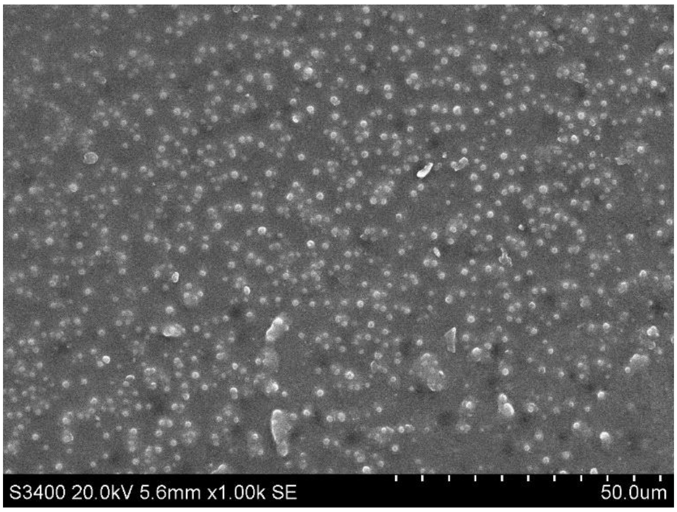

Fig. 5.15 15 wt.% OAPS PDMS top surface area

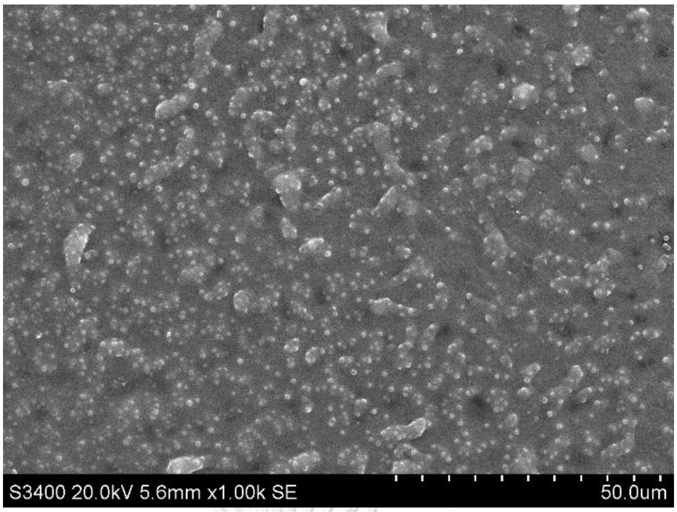

Fig. 5.16 20 wt.% OAPS PDMS top surface area

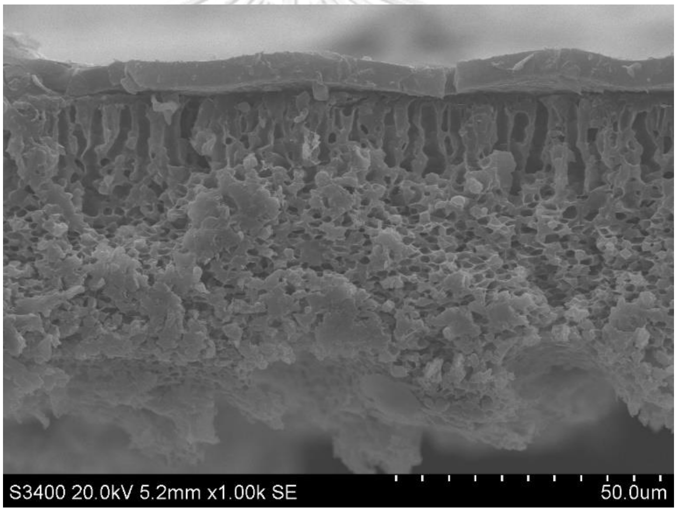

Fig. 5.17 5wt.% OAPS PDMS cross - section

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From Fig. 5.13 - 17, when increased amount of OAPS filler loading from 5 wt.% to 10 wt.%, the increment of density of filler particle on the surface of composite membranes was clearly observed.

The cross – section of filler loading membrane was also characterized as displayed in Fig. 5.17. All composite membranes showed similar morphology, only cross – section area of 5 wt.% OAPS loading was thus selected as the example. The structure of OAPS loading membrane was like the bare PDMS membrane. The top selective layer was clearly isolated from PVDF support layer. The dense selective layer indicated the good dispersion of POSS OAPS and ONPS filler. The thickness of PDMS layer was about 5.12 μm and of PVDF support was 52.06 μm.

The effect of OAPS loading in PDMS on membrane hydrophobicity was further examined (see Fig. 5.18).

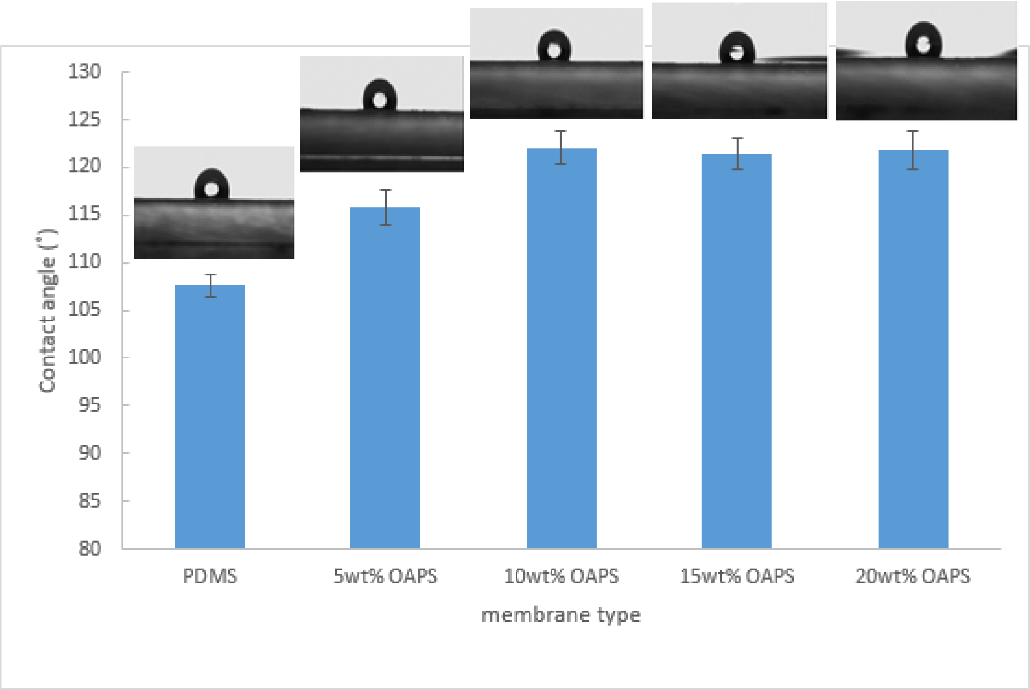

Fig. 5.18 Contact angle of OAPS PDMS at various loading percentages

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At low loading (0 - 10 wt.%) of OAPS, the contact angle of membrane increased and then remained constant at around 122 when more fillers were added. Another factor that played the important role on the contact angle is the surface roughness [40]. If the solid had a very high roughness surface, it would have a higher contact angle [41]. The surface roughness would acted like the barrier blocked the low solubility solution while absorb the desired solution. From Fig. 5.13 - 14, at low OAPS loading (0 – 10 wt.%) the top surface of membrane became more significant rougher that contributed to the increment of contact angle. At the high % loading of OAPS (10 – 20 wt %), the contact angle of membranes did not change.

The separation performance of the prepared membrane with different OAPS loading was demonstrated in Fig. 5.19 to 5.21.

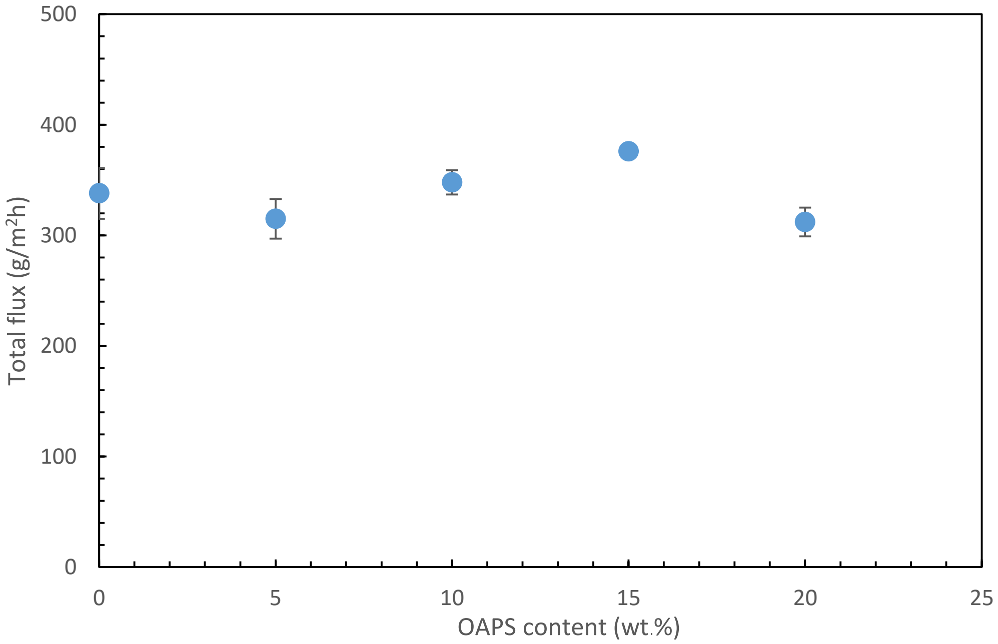

Fig. 5.19 Effect of % filler loading on the total flux

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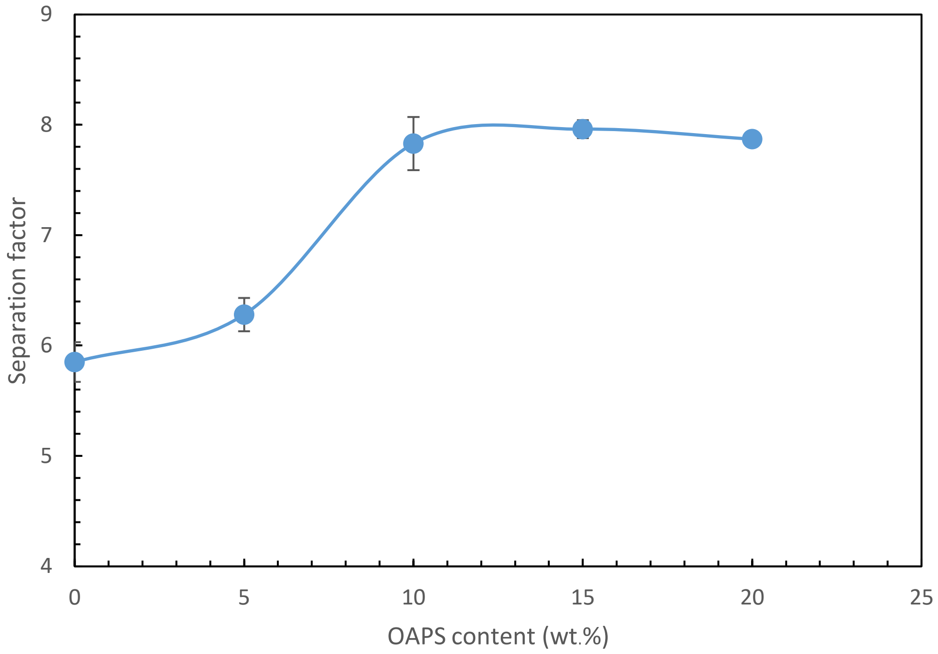

Fig. 5.20 Effect of % filler loading on the separation factor

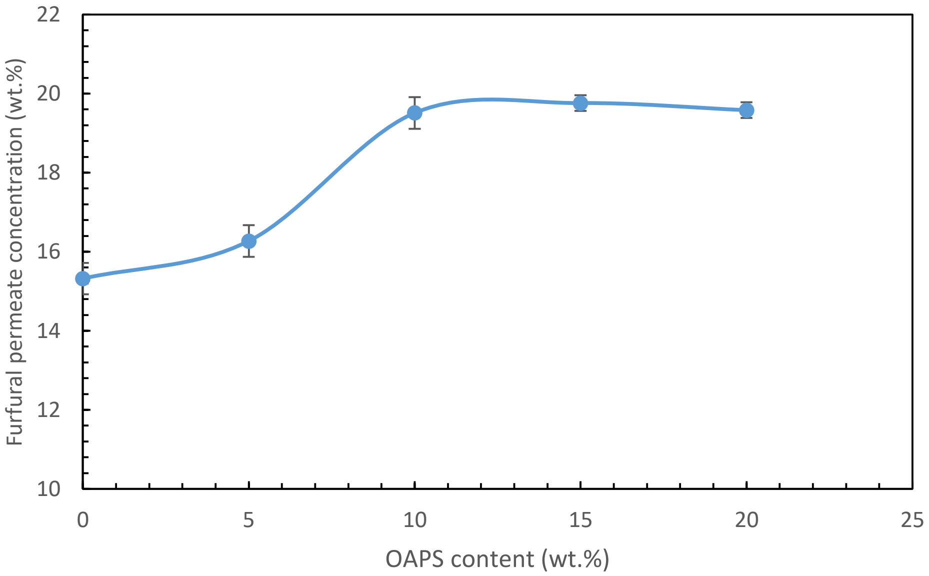

Fig. 5.21 Effect of % filler loading on the furfural permeate concentration

From Fig. 5.19 and 5.20, at low OAPS loading (0 – 10wt%), increasing the amount of OAPS loading could significantly improve the separation factor up to 30 % compared to the bare PDMS membrane. At higher loading (10 – 20 wt.%), the separation factor remained constant at around 7.85. Interestingly, the separation factor followed similar trend as the contact angle (Fig. 5.17) when filler loading increased. This could simply imply that the selectivity of water furfural system was closely related to membrane hydrophobicity. The more hydrophobic or the more organophilic the membrane was, the better interaction between furfural and membrane was achieved. Consequently, the separation factor of membrane was enhanced. For the total flux, the addition amount of OAPS filled into the PDMS did not has a significant impact on the membranes total flux. As the total flux of (0 – 20 wt.%) OAPS loading membranes only changed around 10 % compare to the total flux of bare PDMS membrane. As the result of enhanced furfural selectivity over water, furfural flux was increased but water flux was reduced. As the sum, the total flux remained constant.

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5.4 Effect of feed temperature on the separation performance

The composite membrane with 15 wt% of OAPS was selected to test in the pervaporation process at various feed temperature in order to compare the performance with other membrane types (bare PDMS, commercial PDMS and supporting PVDF layer). The other operating parameters were kept constant (feed concentration at 3wt%, feed rate at 200 ml/min and permeate pressure at 100 mbar). The membrane separation performance was compared in Fig. 5.22 and 5.23.

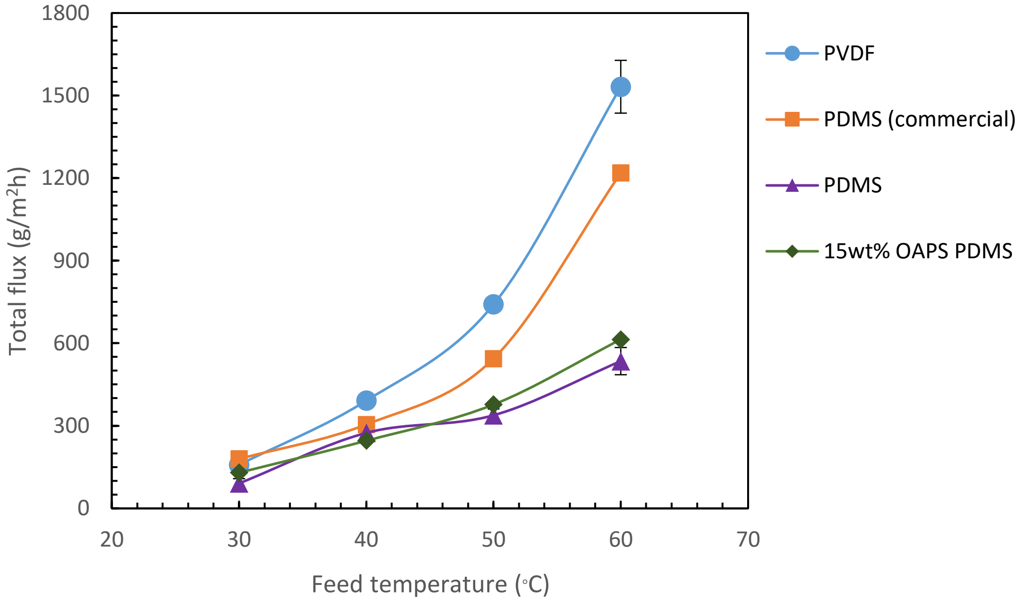

Fig. 5.22 Effect of feed temperature on the total flux

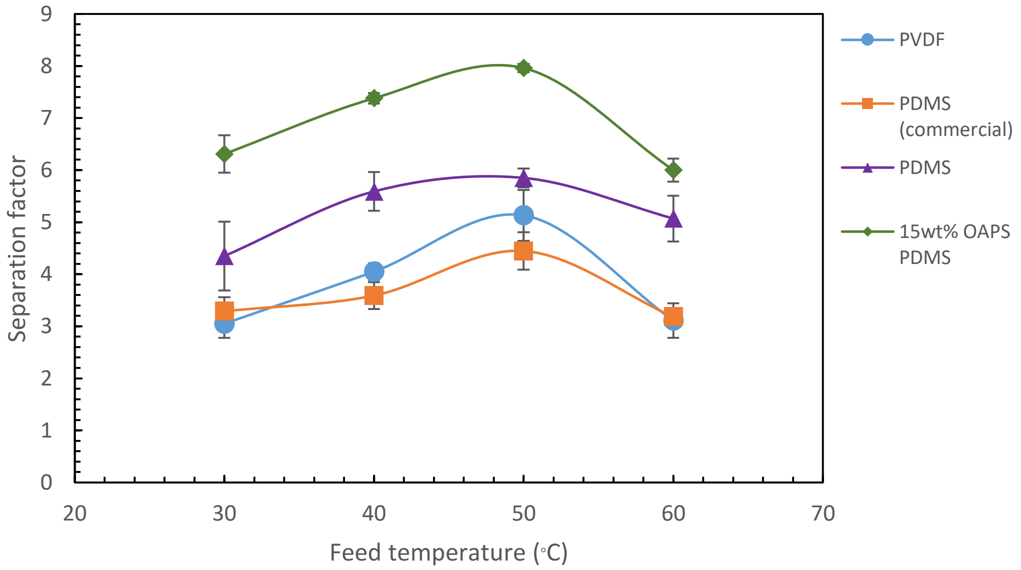

Fig. 5.23 Effect of feed temperature on the separation factor

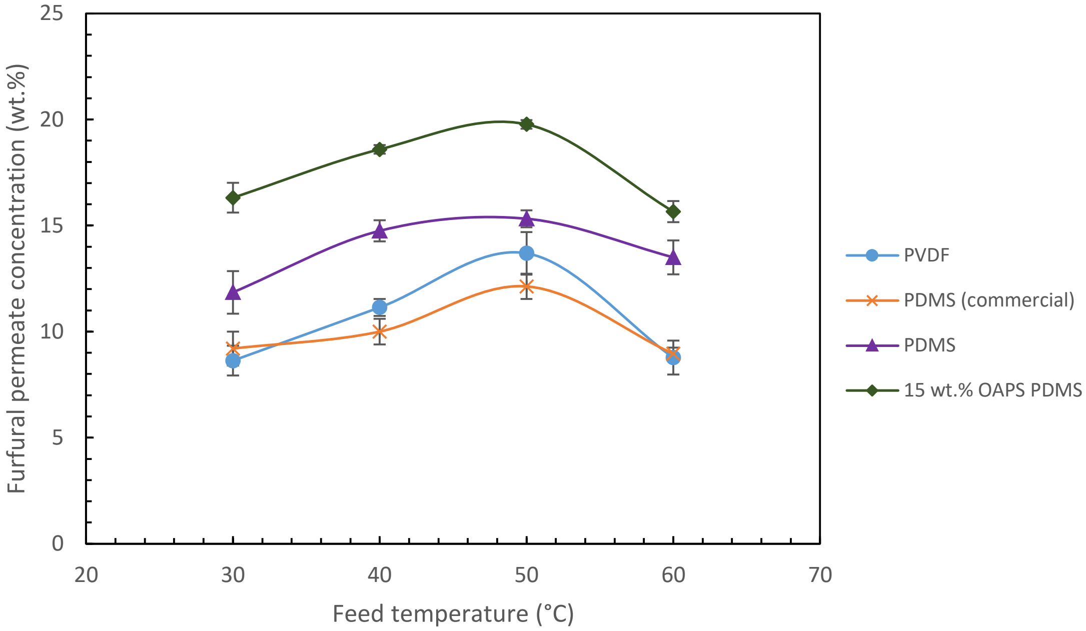

Fig. 5. 24 Effect of feed temperature on the furfural permeate concentration

From Fig. 5.22 and 5.23, with increasing feed temperature, the total flux of membranes increased. There were three reasons to describe the promoted the total flux of membranes. Firstly, the partial vapor pressure of both components was enhanced when the temperature raised, leading to the increase in driving force and it was easier for components to evaporated [1, 2]. Secondly, at higher temperature, the diffusivities of furfural and water were raised. The molecule of furfural and water could diffuse through the membrane faster as they gained the extra kinetic energy, consequently, the total flux of membranes increased [8, 14]. Lastly, the change of polymer chain motions, which increases the free volume between the polymer chain when temperature was raised. The increased free volume allowed both gas molecules to pass through membrane easier.

PVDF support layer had the highest total flux compared to the other membranes. This was because unlike the other membranes, PVDF support did not has an extra mass transfer resistance from top dense selective layer of PDMS., therefore, uncoated PVDF has less mass transport resistance. In addition, the finger – like structure of PVDF support layer also was the reason for the very high flux. The commercial PDMS came in the second place for the highest total flux. The thickness of commercial PDMS was about 35 μm which was thinner than the prepared PDMS (bare and OAPS loading) with film thickness at around 61 μm. The thinner selective layer of membrane resulted in the lower mass transfer resistance for vaporized molecules to pass through [1]. Moreover, very porous morphology of PI layer would significantly contribute the total flux. For the prepared PDMS membrane (bare and OAPS loading), the morphology and thickness of compared membranes were mostly similar; therefore, the total flux of both membranes was not much different.

The separation factor of membranes increased as the temperature was raised from 30 to 50°C and then started to drop at 60°C. This could be explained with two contrary factors: When the feed temperature was increased from 30 to 50°C, it incresed partial vapor pressure of furfural that was more pronounced than the water, resulting in an enhanced driving force and thus increased rate of the furfural flux compare to the water. This led to the higher concentration in furfural permeate and the better separation factor of membranes [2]. On the hand, when the feed temperature was further raised, it enhanced the motion of polymer chain and increased free volumes in membranes structure. The increase free volume and flexibility of polymer chain allowed the molecule of the water and furfural to pass through membrane better and lost their property to separate furfural and water [16]. This observed trend of separation factor from this work was similar to previous reports in literature that the separation factor reached it maximum value at around 65°C of feed temperature and then drop when temperature was further increased [2].

The composite membrane with 15 wt% OAPS showed the best separation factor compare the others, this might be contributed from its high hydrophobicity that had the potential to interact with the furfural. In contrast, PDMS commercial

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membrane had the worst performance in separating furfural and water. This could be described that the hydrophilic polyimide supporting layer of the commercial membrane, having the contact angle below 80° [42], could ruin the separation of water and furfural. Moreover, from the pervaporation performance, the result showed that the bare PVDF support layer itself had the ability to separate furfural and water. The higher contact angle of PVDF could improve the separation ability of the membrane including the higher thickness of PVDF support layer compare to the PI layer. Coating PDMS selective layer over the PVDF support layer made the membrane contact angle became more hydrophobic. Consequently, the prepared PDMS membrane could separate the furfural and water better.

Activation energy of pervaporation

The activation energy of membranes pervaporation could be estimated from the relationship between the component flux and the temperature which usually expressed by the Arrhenius equation [1]. The logarithm of the component flux was plotted against the reciprocal of the feed temperature. The activation was calculated from the slope of the graph as plotted in Fig.5.25 and 5.26. The estimated activation energy of furfural and water flux was summarized in Table 5.2

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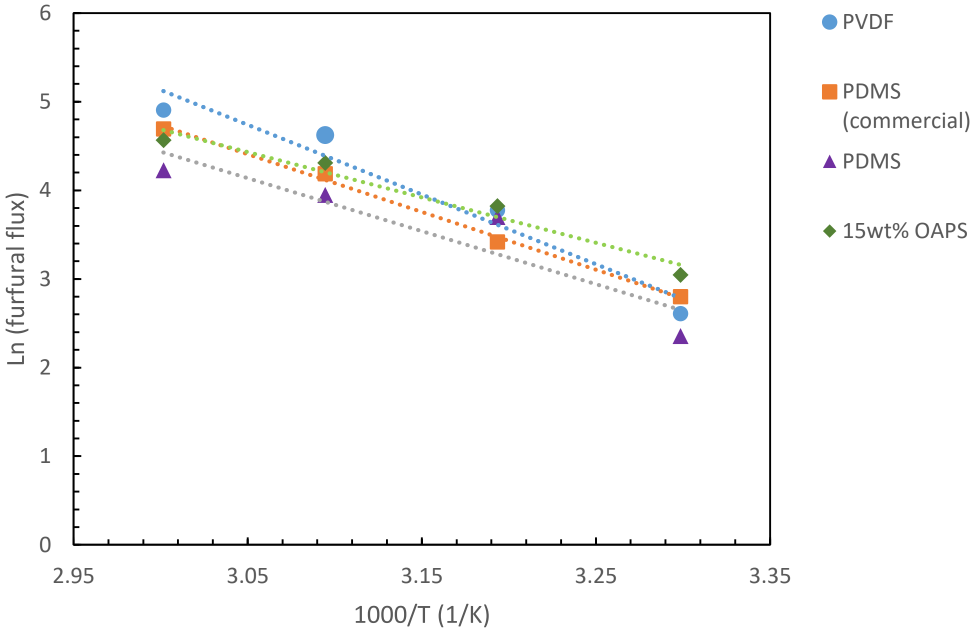

Fig. 5.25 Variation of the natural logarithms of furfural flux with temperature

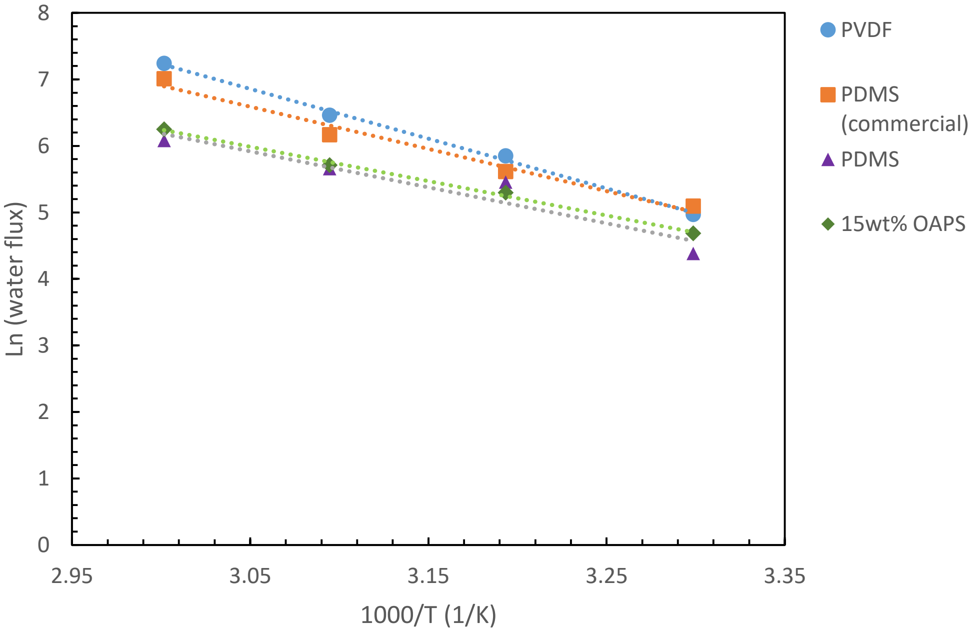

Fig. 5.26 Variation of the natural logarithms of water flux with temperature

Table 5.2 The activation energy of furfural and water

Membrane type	Furfural activation energy (KJ/mol)	Water activation energy (KJ/mol)
PVDF	65.3	62.3
Commercial PDMS	54.2	52.8
PDMS	49.7	44.9
15 wt% OAPS PDMS	42.6	42.9

Generally, if the activation energy of component is low, membranes are willing to let that component to pass through easily [14]. Comparing the furfural and water activation, the activation energy of water was slightly lower than the furfural activation energy was found in PVDF, commercial PDMS and PDMS membranes. Only, membrane with 15 wt% of OAPS showed that the activation energy of furfural was slightly lower than water implied that the permeation of furfural through OAPS PDMS membrane was much easier. It could conclude that, this composite membrane was more selective to the furfural. The positive value of activation energy indicated that the increased of feed temperature would improve the furfural and water flux. Moreover, the high activation energy of PVDF support layer meant that it was more sensitive to the temperature changes [1].

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Chapter 6

Conclusion

6.1 Conclusion

Three types of loading filler (zeolite socony mobil – 5 (ZSM – 5), octaaminophenyl silsesquixane (OAPS) and octanitrophenyl silsesquixane (ONPS)) were incorporated into the polydimethylsiloxane (PDMS) selective layer in order to compare the pervaporation performance for furfural and water separation. The morphology and property of membranes were influenced by the type of fillers and content of filler. ZSM – 5 could not incorporate with the polymer well and aggregated on the top surface. The hydrophilicity of ZSM – 5 resulted in the incompatibility with the hydrophobic PDMS polymer leading to the very poor dispersion and reduction of hydrophobicity. On the other hand, ONPS and OAPS fillers showed the good dispersion on the PDMS selective layer due to the hydrophobic of POSS. OAPS could promote the higher contact angle than ONPS because ONPS filler had the dipole from the coordinate covalent bond which favors interacting with water. The increase of amount OAPS loading could improve the hydrophobic of membrane lead to the rise of contact angle until reached the maximum value at 10 wt% loading of OAPS. At the low amount of OAPS filler loading, the roughness was significantly increased while at the high amount of loading, the surface roughness did not notably changed. The addition of OAPS to the membrane improved the separation factor of the membranes. The hydrophobic nature of OAPS enhanced its interaction with furfural and improved separating performance of the composite membrane. Compared to the commercial membrane, though the composite membrane prepared in this work could provide low permeate flux, the separation factor was much higher. The increase of feed temperature would further improve the total flux of membrane because the partial

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vapor pressure of both components was increased. The polymer chain also became more flexible as the temperature was raised, leading to the easier for water and furfural to pass through the membrane. The separation factor was increased at the temperature ranged 30 – 50 °C then dropped at 60°C. This resulted from the increase of partial vapor pressure of furfural was grew rapidly than the water. While at feed temperature 60°C, the effect of free volume would have more impact over the increased of partial vapor pressure so the separation reduced. The feed rate did not affect the pervaporation performance as the effective area of membrane was quit low. The addition of OAPS also lead to the lower activation energy of furfural that helped improving membranes selectivity.

6.2 Recommendation

The membrane technology still has plenty room for an improvement. Membrane property can be affected by many parameters during the fabrication by the phase inversion. Thus, the uncontrollable factors like moisture, room temperature and the casting speed could affect the structure of the resultant membrane. These problems may be fixed by the more advanced technique such as the auto membrane casting application with controllable ambient condition.

The other interesting filler type or polymer may give the better separation performance. The new technique like polymer blend or addition of functional chemicals to the filler are yet to study.

The thickness of the PDMS selective layer may be the key factor for the membrane. If the higher thickness could be prepared on the support, it would help improving membrane separating performance.

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APPENDIX

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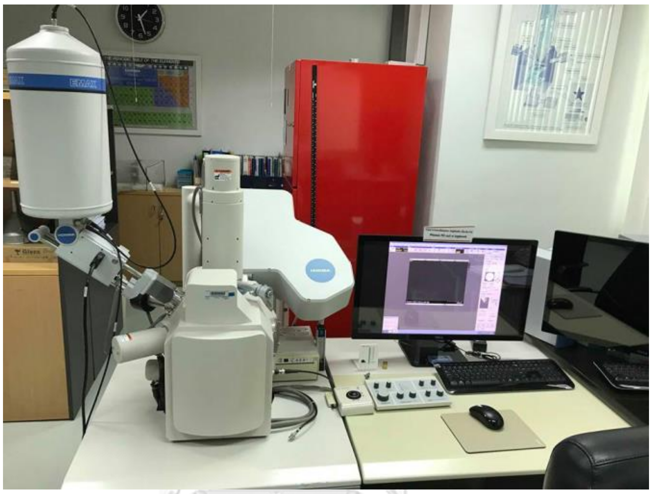
APPENDIX A

Pictures of characterized instruments, membrane preparation tools & pervaporation separation system

1. Scanning Electron Microscope (SEM) – Hitachi S - 3400 N

   SEM was used to study the morphology of fillers and membranes.



2. Ion Sputter – Hitachi – E1010

   Membranes and filler would be coated by the gold for 90 seconds before SEM tested.

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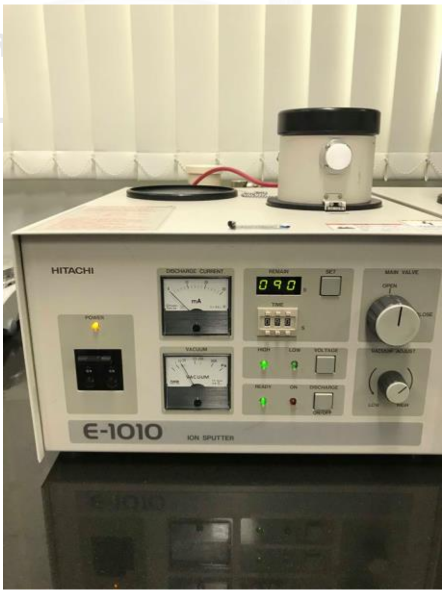
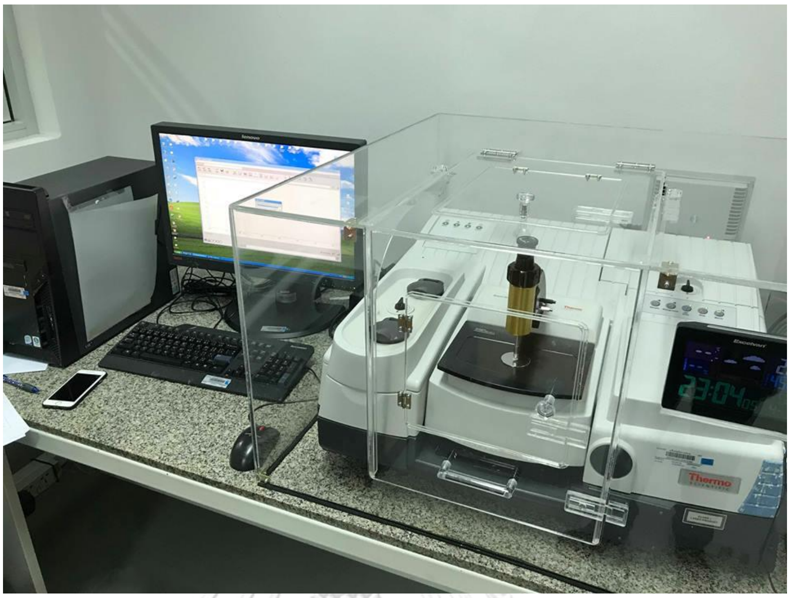


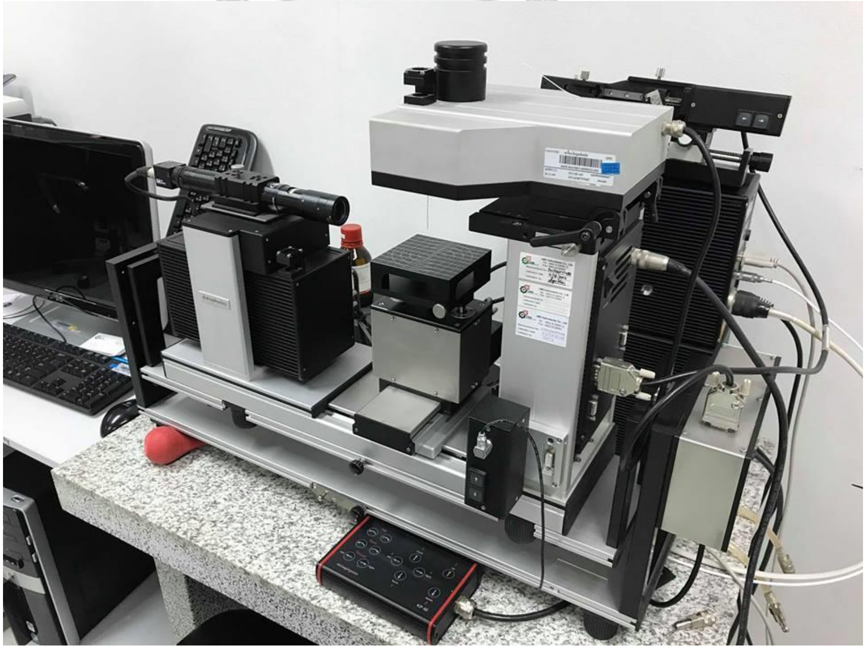
3. Fourier Transform Infared Spectrometer - Attentuated total reflectance (FTIR – ATR) - Nicolet 6700

   The chemical structure of membranes was observed via FTIR – ATR.



4. Contact angle measurement – OCA 40

   The hydrophobicity of membranes was characterized by the contact angle measurement.



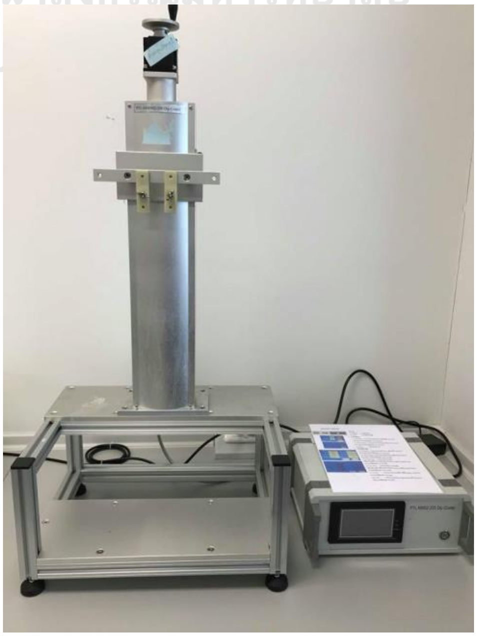
5. High performance liquid chromatography

The concentration of permeate solution was measured by HPLC system with UV and RID detector.

The HPLC column was HPX87 – H. Five molar of sulfuric acid was used as the mobile phase. Total flow of mobile phase was 0.6 milliliter per min while oven temperature was at 45 °C.

6. Membrane dipping machine

The PDMS selective layer was dipped on the PVDF support via this machine.



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7. Pervaporation separation system

The prepared membrane would be test their separation performance in this pervaporation line.

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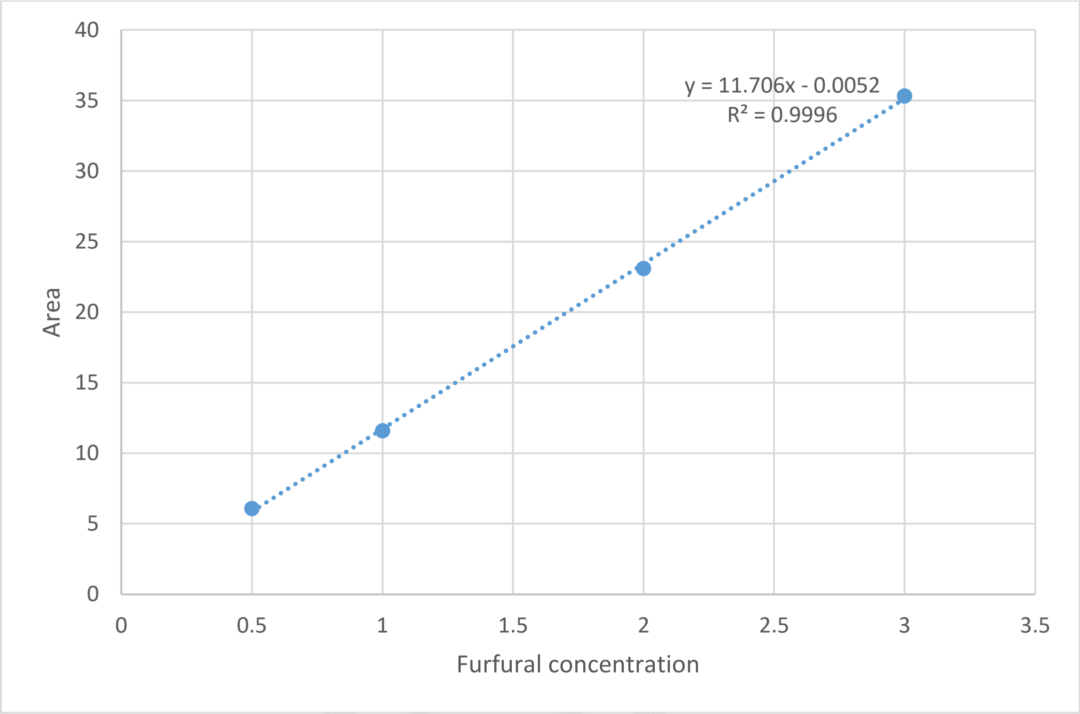
APPENDIX B

Calibration curve of the furfural

The calibration curve of furfural was analyzed by high performance liquid chromatography.



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APPENDIX C

Calculation

Membrane porosity

The PVDF support porosity was calculated in order to find the suitable polymer concentration to fabricate the membrane support.

$$\varepsilon = \frac{m_n/\rho_n}{m_n/\rho_n + m_p/\rho_p} \text{ x } 100\%$$

Where, ε is the porosity of the membrane, m_n is the mass of absorbed water on the wet membrane, m_p is the mass of the dry membrane, ρ_n is the density of water, and ρ_p is the density of polymer.

<u>Example</u>

For 24%wt PVDF support had the mass of absorbed water on wet membrane, mass of dry membrane, density of water and density of polymer equaled 0.0379 g, 0.022 g, 1 g/ml and 1.78 g/ml, respectively.

$$\varepsilon = \frac{\frac{0.0379g}{1\ g/cm^3}}{\left(\frac{0.0379g}{1g/cm^3}\right) + \left(\frac{0.022g}{1.78g/cm^3}\right)} \times 100\%$$

$$= 75.41\%$$

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Feed solution prepared

The 3 wt% of furfural feed was prepared by mixing the furfural (purity 99%, density 1.16 g/cm^3) and DI water type 1.

Feed solution 1 liter (density of 3wt% mixing solution about 1.004 g/cm^3)

Feed solution weight = density mixing solution X feed solution volume

= 1.004 g/cm^3 X 1,000 cm^3

= 1,004 g.

Mass of furfural at 3wt% concentration = $\frac{3}{100}$ X 1,004 g = 30.12g

Volume of furfural at 3wt% concentration = $\frac{mass\ furfural}{density\ of\ furfural}$

$= \frac{30.12g}{1.16\ g/cm^3}$

$= 25.96\ cm^3$

Furfural 99% purity $= \frac{100}{99}$ X $25.96\ cm^3 = 26.22\ cm^3$

To prepared 3wt% furfural feed concentration 1 liter, 26.22 cm^3 from the commercial grade need to be added.

Pervaporation performance

The membrane separating performance was determined by the total flux and separation factor. They could be calculation through this equation.

$$J = \frac{Q}{At}$$

Where J is the flux (g/m^2h), Q is the weight of permeate obtained at time t and A is the effective membrane area.

$$\alpha_p = \frac{C_{i2}}{C_{i1}} \frac{C_{j1}}{C_{j2}}$$

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$$\alpha_P = \frac{Y(1-X)}{X(1-Y)}$$

α_p is the separation factor for permeation of the solute where C_{i1} and C_{i2} are the concentration of the solute in feed and permeate, respectively. C_{j1} and C_{j2} are the concentration of solvent (water) in feed and permeate, respectively. X is weight faction of furfural in feed and Y is weight faction of furfural in permeate.

<u>Example</u>

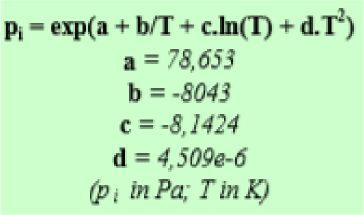
For 15wt% OAPS operated at feed temperature 30°C , feed concentration 3wt%, permeate pressure 100 mbar, feed rate 200 ml/min and the effective area was 15.21 cm^2. In 1 hour, the solution that could gained at the cold trap was 0.21g. The permeate concentration of furfural that characterized by HPLC was 15.59 wt%.

$$\text{Total flux} = \frac{0.21g}{15.21cm^2 \times 1\ hour} \times \frac{10{,}000cm^2}{1m^2} = 138.06\ \text{g/m}^2\text{h}$$

$$\text{Separation factor} = \frac{15.59\ wt\% \times 97\ wt\%}{3\ wt\% \times 84.41\ wt\%} = 5.97$$

Furfural and water vapor pressure

The vapor pressure of furfural was calculation by using the Antoine equation while the vapor pressure of water could be referred from the other researches.



$p_i = \exp(a + b/T + c.\ln(T) + d.T^2)$

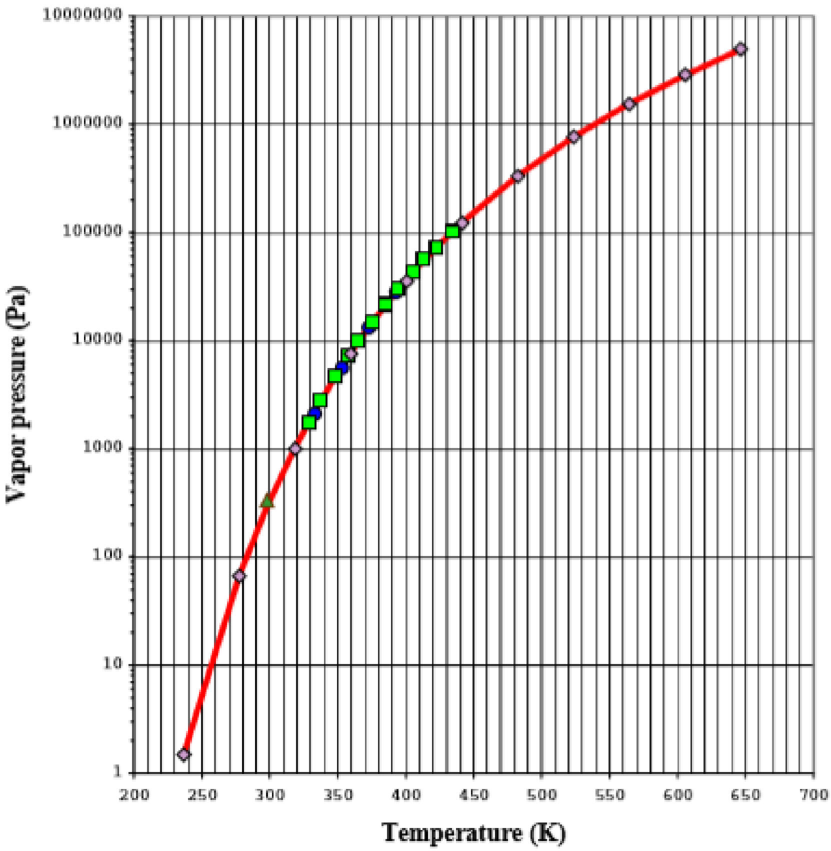
a = *78,653*

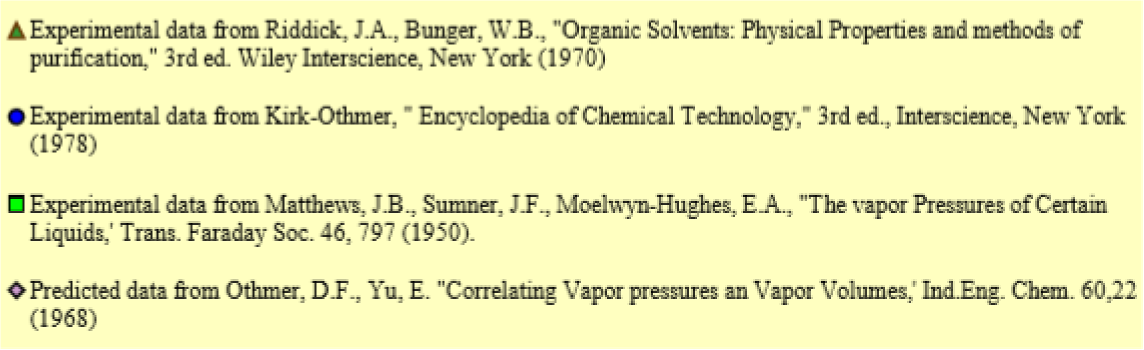
b = *-8043*

c = *-8,1424*

d = *4,509e-6*

(p_i in Pa; T in K)





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◆ Predicted data from Othmer, D.F., Yu, E. "Correlating Vapor pressures an Vapor Volumes,' Ind.Eng. Chem. 60,22 (1968)

<u>Example</u>

At 30 °C

$= \text{exponential } (78{,}653+\frac{-8043}{303.15}+(-8.1424)\ln 303.15+(4.509e^{-6})(303.15)^2)$

$=406.84$ Pascal

The activation energy of furfural and water

The activation of furfural and water in the membranes could be calculated by using the slope of the graph plotted between the logarithm of the total flux and the reciprocal of the feed temperature.

$$J_i = J_{i,0} \exp\left(\frac{-E_{a,i}}{RT}\right)$$

Where J_i is the permeation flux of component i (g/m^2h), $J_{i,0}$ is the pre-exponential factor of component I (g/m^2h), $E_{a,i}$ is the activation energy of component I (kJ/mol), R is the gas constant (8.314 J/mol·K) and T is the feed temperature (K).

$$\ln J_i = \ln J_{i,0} - \frac{E_{a,i}}{RT}$$

$$Y = mX+C$$

$$Y = \ln J_i \ (-)$$

$$X = \frac{1}{T} \ (K^{-1})$$

$$m = -\frac{E_{a,i}}{R} \ (K)$$

<u>Example</u>

The slope of 15% OAPS membrane furfural flux was -5.1251

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$(1{,}000)(-5.1251\text{K}) = -\frac{E_{a,i}}{8.314\ J/molK}$; 1,000 from the multiple 1000/T and slope unit is (Kelvin)

$E_{a,i}$ = 42.61 kJmol^{-1}

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VITA

Mr. Seth Sawatdiruk was born on 25 February 1993 in Trang, Thailand. In 2015, He graduated from the faculty of Chemical Engineering, Mahidol University in Bachelor of Chemical Engineering. He decided to continue his education by joining the Department of Chemical Engineering, Chulalongkorn University as a master degree student. In 2018, He graduated with a thesis entitled "COMPARISON OF ZIF - 8 AND POSS NANOCOMPOSITE PERVAPORATION MEMBRANES FOR FURFURAL/WATER SEPARATION"

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