GRAFTING OF POLY(*N*-ISOPROPYLACRYLAMIDE) (PNIPAM) ONTO NYLON POROUS FILM VIA MICROWAVE-ASSISTED POLYMERIZATION FOR THERMO-RESPONSIVE GATING APPLICATION

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การกราฟท์พอลิเอนไอโซโพรพิลอะคริเอไมด์ลงบนฟิล์มรูพรุนของไนลอนด้วยเทคนิคการสังเคราะห์โดยใช้ไมโครเวฟช่วยสำหรับการใช้งานทางด้านการเปิดปิดของเกทที่ตอบสนองต่อความร้อน

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Suranaree University of Technology has approved this thesis submitted in partial fulfillments of the requirement for a Master's Degree.

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งานวิจัยนี้มีวัตถุประสงค์เพื่อกราฟท์พอลิเอนไอโซโพรพิลอะคริเอไมด์ลงบนไนลอนเมมเบรนโดยการใช้อาร์กอนพลาสม่าสร้างอนุมูลอิสระบนพื้นผิวและใช้ไมโครเวฟช่วยในการให้ความร้อนเพื่อกระตุ้นให้เกิดการกราฟท์ งานวิจัยนี้ประกอบด้วยการศึกษาตัวแปรในขั้นตอนของการใช้ไมโครเวฟเพื่อหาสภาวะที่เหมาะสมสำหรับการกราฟท์ จากนั้นศึกษาผลของปริมาณการกราฟท์และโครงสร้างที่แตกต่างกันของพอลิเอนไอโซโพรพิลอะคริเอไมด์ต่อโครงสร้างจุลภาคและสมบัติในการตอบสนองต่อความร้อนของเมมเบรน รวมไปถึงประสิทธิภาพในการเป็นเกทเปิด-ปิดสำหรับการซึมผ่านของน้ำ ในการศึกษาสภาวะที่เหมาะสมที่สุดในการสังเคราะห์ มีตัวแปรที่สำคัญได้แก่ กำลังไฟและเวลาในการฉายรังสีของไมโครเวฟโดยศึกษาในช่วง 100 ถึง 800 วัตต์ และระยะเวลา 5 ถึง 15 นาที ตามลำดับ ในการหาปริมาณการกราฟท์จากการชั่งน้ำหนักพบว่า การกราฟท์จะเกิดขึ้นเมื่ออุณหภูมิมากกว่า 85 องศาเซลเซียสและปริมาณการกราฟท์จะเพิ่มขึ้นตามอุณหภูมิที่สูงขึ้นซึ่งเป็นผลมาจากกำลังไฟและเวลาในการให้ความร้อนด้วยไมโครเวฟที่เพิ่มขึ้น อย่างไรก็ตามจากการศึกษาลักษณะโครงสร้างในระดับไมโครเมตรของเมมเบรนที่ได้จากกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด พบการเสียสภาพของเมมเบรนเมื่อผ่านการให้ความร้อนด้วยไมโครเวฟภายใต้กำลังไฟ 800 วัตต์เป็นเวลา 15 นาที เนื่องมาจากความร้อนที่สูงเกินอุณหภูมิที่เมมเบรน สามารถใช้งานได้ ดังนั้นเพื่อป้องกันการเสียสภาพของเมมเบรน การกราฟท์ด้วยไมโครเวฟที่กำลังไฟ 800 วัตต์ และเวลา 10 นาที จึงถูกเลือกเป็นสภาวะที่เหมาะสมที่สุดในการกราฟท์ครั้งนี้

ในการศึกษาผลของปริมาณและโครงสร้างของพอลิเอนไอโซโพรพิลอะคริเอไมด์ที่ถูกกราฟท์บนเมมเบรน โดยใช้สารละลายของมอนอเมอร์ที่มีการเติมและไม่เติมตัวเชื่อมขวาง มีความเข้มข้นของเอนไอโซโพรพิลอะคริเอไมด์มอนอเมอร์จาก 2 3 5 7 ถึง 10 เปอร์เซ็นต์โดยน้ำหนัก พบว่าปริมาณมอนอเมอร์ที่เพิ่มขึ้นส่งผลต่อปริมาณการกราฟท์ที่เพิ่มขึ้น พอลิเมอร์ที่ถูกกราฟท์ส่วนใหญ่จะอยู่บนพื้นผิวนอกและทางเข้าของรูพรุนบนเมมเบรน โดยมีความหนามากขึ้นและสังเกตได้ชัดเจนยิ่งขึ้นเมื่อปริมาณการกราฟท์เพิ่มสูงขึ้น ส่วนในการเติมสารเชื่อมขวางนั้นจะทำให้โครงสร้างของสายโซ่พอลิเมอร์ที่ถูกกราฟท์มีลักษณะเป็นร่างแหเชื่อมโยงกัน สำหรับประสิทธิภาพในการทำ

หน้าที่เป็นเกทปิดเปิดควบคุมการผ่านเข้าออกของน้ำจะถูกทดสอบจากการวัดฟลักซ์ของน้ำที่ซึมผ่านเมมเบรน โดยทดสอบทั้งการไหลแบบขนานและแบบตั้งฉากกับเมมเบรน เมื่ออุณหภูมิของน้ำมีการเปลี่ยนแปลงอยู่ในช่วง 25 ถึง 45 องศาเซลเซียส เมื่อปริมาณการกราฟท์เพิ่มขึ้น ฟลักซ์ของน้ำที่วัดได้จะมีค่าลดลงเนื่องมาจากพอลิเอนไอโซโพรพิลอะคริเอไมด์ถูกกราฟท์ลงบนพื้นผิวทางเข้าและภายในของรูพรุน ทำให้ขนาดของรูพรุนเล็กลง น้ำจึงซึมผ่านได้น้อยลง อย่างไรก็ตาม เมื่อปริมาณการกราฟท์สูงมากเกินไป พอลิเอนไอโซโพรพิลอะคริเอไมด์ที่ถูกกราฟท์จะไม่สามารถทำหน้าที่เป็นเกทเปิดปิดได้ เนื่องจากพอลิเอนไอโซโพรพิลอะคริเอไมด์ไปอุดตันทางเข้าของรูพรุนบนเมมเบรน ในการศึกษาผลของโครงสร้างของพอลิเอนไอโซโพรพิลอะคริเอไมด์ 2 แบบได้แก่ โครงสร้างแบบเส้นกับโครงสร้างแบบร่างแห จากการเปรียบเทียบที่ปริมาณการกราฟท์เท่ากันพบว่า โครงสร้างแบบเส้นมีสมบัติในการเป็นเกทควบคุมการเปิดปิดได้ดีกว่า ในช่วงอุณหภูมิการละลายวิกฤตของพอลิเอนไอโซโพรพิลอะคริเอไมด์ที่ 32 องศาเซลเซียส เนื่องจากปลายสายโซ่พอลิเมอร์พอลิเอนไอโซโพรพิลอะคริเอไมด์มีอิสระสามารถตอบสนองต่อการเปลี่ยนแปลงอุณหภูมิได้อย่างรวดเร็ว ในขณะที่โครงสร้างแบบร่างแหตอบสนองต่ออุณภูมิของน้ำได้ช้าและน้อยมาก นอกจากนี้ในการทดสอบประสิทธิภาพในการใช้ซ้ำได้ โดยนำเมมเบรนของโครงสร้างพอลิเมอร์ทั้งสองแบบที่มีสัมประสิทธิ์ในการทำหน้าที่เป็นเกทเปิดปิดสูงสุด ไปทำการทดสอบการไหลผ่านของน้ำที่อุณหภูมิ 25 และ 40 องศาเซลเซียส วนซ้ำ 10 รอบพบว่าพอลิเอนไอโซโพรพิลอะคริเอไมด์เกทแบบเส้นสามารถนำไปใช้ซ้ำได้ ถึงแม้ในจำนวนรอบที่มากขึ้น จะทำให้ฟลักซ์ลดลงเล็กน้อยเมื่อเทียบกับโครงสร้างแบบร่างแหที่มีฟลักซ์ลดลงอย่างมากจนมีค่าเข้าใกล้ศูนย์ในจำนวนรอบที่น้อยซึ่งสามารถสังเกตเห็นได้ชัดเจนจากการทดสอบด้วยการไหลของน้ำแบบขนาน

ในการนำเมมเบรนฉลาดนี้ไปประยุกต์ใช้งานสำหรับการแยกน้ำและน้ำมันในระบบอิมัลชั่น จากการศึกษาพบว่าเมมเบรนมีความสามารถในการแยกอิมัลชันของน้ำมันในน้ำได้อย่างดีเยี่ยม เมื่อเปรียบเทียบผลของโครงสร้างพอลิเอนไอโซโพรพิลอะคริเอไมด์เกทกับปริมาณการกราฟท์พบว่า ปริมาณการกราฟท์เป็นปัจจัยหลักที่มีอิทธิพลต่อกระบวนการแยก โดยการเพิ่มขึ้นของปริมาณการกราฟท์จะส่งผลให้ประสิทธิภาพในการแยกดีขึ้น โดยสามารถแยก 5 เปอร์เซ็นต์ของน้ำมันมะกอกในน้ำได้ประสิทธิภาพสูงถึง 99.66 เปอร์เซ็นต์ ด้วยเหตุนี้ เมมเบรนฉลาดที่ได้จากการศึกษาครั้งนี้จึงเป็นตัวเลือกหนึ่งที่มีประสิทธิภาพในการใช้แยกน้ำและน้ำมันออกจากกันได้ อีกทั้งกระบวนการสังเคราะห์เมมเบรนดังกล่าวที่ได้จากงานวิจัยนี้ยังถือเป็นวิธีการแบบใหม่ที่ลดการใช้สารเคมีอันตราย รวดเร็ว ประหยัดพลังงานและเวลาที่ใช้ในการสังเคราะห์

สาขาวิชา วิศวกรรมพอลิเมอร์ ลายมือชื่อนักศึกษา พุธิตา เกศศิริพงษ์ษา
ปีการศึกษา 2562 ลายมือชื่ออาจารย์ที่ปรึกษา T. Trongsatitkul

PUTITA KATESRIPONGSA : GRAFTING OF POLY(*N*-ISOPROPYLACRYLAMIDE) (PNIPAM) ONTO NYLON POROUS FILM VIA MICROWAVE-ASSISTED POLYMERIZATION FOR THERMO-RESPONSIVE GATING APPLICATION. THESIS ADVISOR : ASST. PROF. TATIYA TRONGSATITKUL, Ph.D., 100 PP.

POLY(*N*-ISOPROPYLACRYLAMIDE)/THERMO-RESPONSIVE POLYMER
MICROWAVE-ASSISTED POLYMERIZATION/OIL-WATER SEPARATION
POROUS NYLON-6 (N6) MEMBRANE

The purpose of this work was to graft PNIPAm onto Nylon membrane using plasma peroxide technique coupled with microwave-assisted polymerization method. Effect of key parameters including microwave output power and irradiation time on grafting performance were investigated. For grafting optimization, the output power and time of microwave irradiation were varied from 100-800 watts and 5-15 minutes, respectively. The effective grafting yield was achieved when the grafting temperature up to 85°C. Microstructures of the PNIPAm grafted Nylon membrane from Scanning electron microscope (SEM) revealed the membrane fracture after microwave irradiation under 800 watts for 15 minutes. This was attributed to over heat to above the service temperature of the Nylon membrane (135°C). Therefore, the microwave irradiation under 800 watts for 10 minutes was the optimum condition for this grafting technique. Effect of grafted PNIPAm structure and grafting yield on thermo-responsive gating characteristics were investigated. Using the optimum condition for microwave irradiation, monomer concentration was varied from 2, 3, 5, 7, to 10 wt% with and without crosslinker. When NIPAm content increasing, the grafting yield increased in both PNIPAm structures. The grafted PNIPAm chains located mainly on the top surface and the pore entrance of the membrane. The PNIPAm chains also grafted on the inner pore surface when grafting yield increasing. The thermo-responsive gating performance was achieved from the water permeation experiment. The water flux control ability of temperature response in the range of 25-45°C was measured under 100 kPa of operating pressure in cross-flow and direct flow. When the grafting yield increasing, the water flux decreased because of smaller pore sizes. At the same grafting yield, the linear PNIPAm gate effectively opened and closed across the lower critical solution temperature (LCST) of PNIPAm (32°C). The linear PNIPAm chains with free ends could respond quickly to the feedwater temperature. While the crosslinked PNIPAm network structure was compact and slowly responded to the temperature. In addition, the repeatability linear and crosslinked PNIPAm grafted membranes were investigated. Both in cross flow and direct flow, the linear PNIPAm gate was the stable and repeatable thermo-responsive open-close switch performance. Compared to the crosslinked PNIPAm structure, water flux was nearly zero in fast within a small number of the run in the cross-flow mode.

In the application of this smart membrane, the efficiency of oil-water separation was investigated. The linear grafted membrane was able to separate the oil in water emulsions with high efficiency of 99.7%. Therefore, this smart membrane was a good choice for oil-in-water emulsion separation. In addition, the novel grafting technique was also considered green and rapid synthesis which brought a new possibility to fabricate more smart membranes for other applications.

School of Polymer Engineering Student's Signature พุธิตา เกดศรีพรชัยดา

Academic Year 2019 Advisor's Signature T. Trongsatitkul

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CHAPTER I

INTRODUCTION

1.1 General introduction

Stimuli-responsive polymers, also known as "Smart polymers", are polymers that respond with a considerable change in their properties to different stimuli or changes in the environment. The type of smart polymer could be classified according to the stimulus. It responds to the stimuli include physical, chemical and biological stimuli. Phisical stimuli are temperature, light, magnetic and electric. Chemical stimuli are pH, redox and solvent. For biological stimuli, glucose and enzyme are studied. These smart polymers could be useful for various applications such as biomedical engineering, bioseparation, chemical separation, self-healing, anti-fouling, chemical sensors, and tissue engineering. Thermo-responsive polymer, among the other stimuli-responsive polymers, is one of the most intensive studied. This is due to the ease of design and artificially control of the environmental temperature stimulus. Poly(*N*-isopropylacrylamide) or PNIPAm is a thermo-responsive polymer that has been widely studied. This polymer, in the linear form, exhibits the lower critical solution temperature (LCST) at around 32°C in aqueous solutions (Xie, Li, & Chu, 2007). In other words, when the temperature below the LCST of PNIPAm, the polymer dissolves in an aqueous solvent, such as water, indicating that the amide group of polymer chains interact with water molecules and form hydrogen bond. As the temperature arises to and above the LCST, PNIPAm chains collapse and separate from the aqueous solvent. At this state, the chains turn into a globular shape. This behavior is called coil-globule transition. Due to the unique temperature sensitivity, PNIPAm has been thought to be usedfule in medical field. It has been investigated for thee applications such as controlled drug release (Chung-Yang, Trong-Ming, & Wen-Yen, 2009), tissue engineering (Stile & Healy, 2001), and immobilization of enzymes (Gawlitza, Georgieva, Tavraz, Keller, & von Klitzing, 2013). Besides PNIPAm linear chains, PNIPAm can be formed into a three-dimensional crosslinked network and becomes a PNIPAm hydrogel. The crosslinks prevent the hydrogel to dissolve but swell when brought into contact with water. Almost at the same temperature for LCST of the linear PNIPAm, the PNIPAm hydrogel undergoes volume change at the transition temperature. This transition temperature is called volume phase transition temperature or VPTT where the hydrogel turns from a swollen hydrated state to a shrunken dehydrated state (Constantin, 2011). Several studies have been conducted to investigate the technique used for synthesis PNIPAm hydrogels and their composites as well as their mechanical properties, stimuli sensitivities and responsiveness.

Over the last decade, a maked increase in attention has been drawn to thermo-responsive membranes. This is due to their ability to control or adjust permeability in response to a thermal stimulus. Several porous membranes and thermo-responsive functional gates have been investigated. Also, several methods have been developed to prepare thermo-responsive membranes. The methods include both chemical and physical techniques. The chemical technique has been a preferable choice for grafting of thermo-responsive polymers onto porous membrane substrates. The chemical grafting techniques include but not limit to plasma-induced graft polymerization

(PIGP), UV radiation induced grafting, atom transfer radical polymerization (ATRP), plasma graft copolymerization, plasma-graft pore-filling polymerization. Another simple approach to prepare thermoresponsive membranes is fabricating thermo-responsive hydrogels inside the pores of porous membranes (P.-F., X.-J., L.-Y., & R., 2006). However, the membrane with crosslinked gels in the pores possesses a poor gating performance due to a low water diffusivity in the gel which caused by a chain mobility restriction of the crosslinked network. In contranst, the membranes grafted with linear chains have mobile ends which can respond to an environmental stimulus faster than that of with hydrogels filled (Takeo, Akiko, Shin-ichi, & Shoji, 1996). Microwave-assisted polymerization is another technique that has gained significant attention to be used in grafting of PNIPAm onto a porouse membrane. There are several unique advantages in using microwave irradiation such as low energy consumption and thermal homogeneity (Oliver, 2004). For example, microwave-assisted polymerization was used to synthesize hydrogels. PNIPAm microgel was prepared under microwave irradiation, which shortened the reaction time from 6 h to as low as 1 h (Murray et al., 1994).

Many stimuli-responsive gating membranes have been developed. Different functional polymers were grafted onto various porous membrane substrates such as PNIPAm-*g*-HDPE (Yamaguchi, Ito, Sato, Shinbo, & Nakao, 1999), PNIPAm-*g*-PP (Liang, Shi, Viswanathan, Peurrung, & Young, 2000), PNIPAm-*g*-PVDF (Yang et al., 2006), PNIPAm-*g*-PC (Ohashi, Chi, Kuroki, & Yamaguchi, 2016), and PNIPAm-*g*-Nylon-6 (Yang et al., 2006) membranes.

Nylon membrane has been used as a substrate in many studies. Because of its hydrophilic nature and a unique microstructure, Nylon membrane can be effectively grafted and yield a thermo-responsive membrane with a high gating performance. The hydrophilicity of Nylon allows water to permeate through the membrane with higher flux as compared with other membrane (Yang et al., 2006). The Nylon-6 substrate features porous honeycomb structure below the skin layer. This honeycomb structure helps in effective grafting of PNIPAm inside the pores across the membrane thickness. With these reasons, Nylon porous membrane was chosen to be used as a substrate for preparing thermo-responsive gating membrane in our present work.

In the present study a novel technique has been developed to graft PNIPAm on to Nylon membranes. Plasma peroxide method together with microwave-assisted polymerization was utilized to fabricate the gating membranes of PNIPAm grafted onto Nylon porous substrates. In order to obtain optimum condition of grafting, the results of the microwave irradiation time and output power were investigated. Furthermore, the monomer content was varied to obtain different grafting yield then investigate the gating characteristics of the membranes. In this study, the focus was on optimization of grafting PNIPAm onto surface of Nylon-6 membrane. The resulting grafted membranes were going to be investigated for their thermo-responsive gating characteristics in response to temperature change. The thermo-responsive gating characteristics and gating performance of grafted membranes were evaluated by determining the thermo-responsive water permeability. Moreover, a hydrophilic membrane was suitable for separating oil-in-water emulsions, while a hydrophobic membrane separated water-in-oil emulsions. This smart membrane with switchable hydrophilicity and hydrophobicity may be considered feasible for oil-water separation.

1.2 Research objectives

The main objectives of this study are as below :

(i) To synthesize the PNIPAm grafted Nylon membrane by plasma peroxide method together with microwave-assisted polymerization.

(ii) To optimize the condition of microwave-assisted polymerization (irradiation time, output power, and monomer concentration).

(iii) To investigate thermo-responsive gating characteristics of the PNIPAm grafted Nylon membrane.

(iv) To investigate reversibility and repeatability of thermo-responsive open-close gating switch of the PNIPAm grafted Nylon membrane.

1.3 Scope and limitation of the study

The Nylon membranes purchased from Whatman Co., with an average pore size of 0.2 µm and thickness of 150-187 µm, were used in this study. Specific surface area and total pore volume of the Nylon membrane were evaluated using Brunauer-Emmett-Teller (BET) surface area analysis. Before graft polymerization, Nylon membrane was treated with surface plasma technique under argon gas at 30W for 60 s. Then the treated membrane was kept in dry and dark place for 2 days to generate peroxide on surface. The microwave-assisted polymerization was performed in a commercially available microwave oven with output power of 100-800 W. Optimum condition of grafting was first investigated using a constant monomer concentration at 10 wt% with and without the presence of crosslinker. The membranes were irradiated by microwave irradiation using for 5-15 min. After that, the monomer solution contents were 2, 3, 5, 7, and 10 wt% of the aqueous solution which could be grafted in the optimum condition.

Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) was used to confirm the PNIPAm grafted onto the Nylon membrane. Mass of membrane both before and after grafting were used to determine the grafting yield of PNIPAm on the membrane substrate.

The morphologies of the Nylon-6 and PNIPAm grafted Nylon membranes were examined using a scanning electron microscope (SEM). The contact angle of the membranes was determined using a contact angle goniometer (Dino-Lite Digital Microscope, Taiwan). Thermo-responsive gating characteristics and gating performance of PNIPAm grafted Nylon membrane were investigated using a water filtration apparatus under an operating pressure of 100 kPa. The effective membrane area for water permeation was 11.34 cm^2. Water fluxes through different membranes at different temperatures in ther range of 25 to 45°C were measured. The result of the water flux was used as an indication of the pore closing and opening due to the thermo-responsiveness of the grafted linear PNIPAm chains and crosslinked PNIPAm networks. The separation of oil-in-water emulsions was investigated as to represent one way of utilization of this smart membrane. The emulsions were prepared with different oils (paraffin, and olive oil) by mixing with Tween 20 as a surfactant under strong magnetic stirring and shaken to obtain a milky solution. The separation was achieved using a microfiltration apparatus by gravity only.

CHAPTER II

LITERATURE REVIEW

The main focus of this study is to synthesize PNIPAm grafted Nylon membranes using the microwave-assisted polymerization. There are several parameters that can influence the synthesis : chemical composition, grafting temperature, grafting time, microstructure of membrane, and surface modification. To shorten the grafting time, microwave-assisted polymerization was applied for the grafting step. Comparing with the conventional thermal heating, the reaction time can be shortened about six times (Shi & Liu, 2006). Furthermore, microwave heating can eliminate the wall effects caused by temperature gradients, which normally occur in conventional heating methods, such as oil-bath heating and water-bath heating. To modify the surface, plasma treatment was used before grafting. Plasma treatment has been used in many studies as a part of plasma-induced graft polymerization (PIGP). The challenge is to combine the two techniques from the different polymerization method while maintain the properties of Nylon membrane under microwave irradiation. Several studies on the synthesis of PNIPAm grafted on various membranes, their gating performance, principles of microwave-assisted polymerization, and principles of PIGP have been reported. However, microwave-assisted heating for PNIPAm grafting and the membrane properties from this method have not been investigated before.

2.1 Poly(*N*-isopropylacrylamide)

Poly(*N*-isopropylacrylamide) or PNIPAm is a thermo-responsive polymer with inverse solubility and a reversible phase transition upon heating. It is synthesized from commercially available monomer of *N*-isopropylacrylamide. In general, some thermal responsive polymer exhibits a lower critical solution temperature (LCST), below which the polymer is soluble in an aqueous solution. When the temperature is raised above the LCST, the polymer first undergoes a phase transition; the polymer chains collapse and form aggregates. This phenomenon is reversible such that when the temperature is lowered, the polymer chains once again become soluble. Linear PNIPAm has a LCST of approximately 32°C. It is soluble at room temperature and phase separates from water near the body temperature (37°C). Many studies have been used PNIPAm as a linear polymer (Humphreys, Willott, Murdoch, Webber, & Wanless, 2016), a hydrogel (Gawlitza et al., 2013), or a copolymer (Ito et al., 2002). The schematic of chemical structure for PNIPAm was shown in Figure 2.1. NIPAm monomer possesses two characteristic moueties which are amide (—CONH—) and propyl (—$CH(CH_3)_2$) in the structure. At the temperature below LCST, Chains of PNIPAm exist in a coil configuration due to the hydrogen bonding between amide groups and water molecules. At the temperature above LCST, the hydrogen bonds are weak as the kinetic energies of the polymer molecules become higher than the energy of hydrogen bonding of water with the polymer molecules. Thus, hydrophobic interactions between the hydrophobic backbone and iso-propyl groups become prominent. Consequently, polymer conformation changes from linear PNIPAm coils to the collapsed globules (Figure 2.2) due to an intermolecular aggregation of hydrophobic moieties.

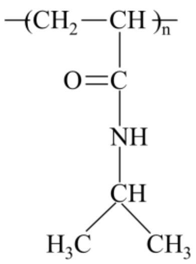


Figure 2.1 Chemical structure of poly(*N*-isopropylacrylamide) (Humphreys et al., 2016)

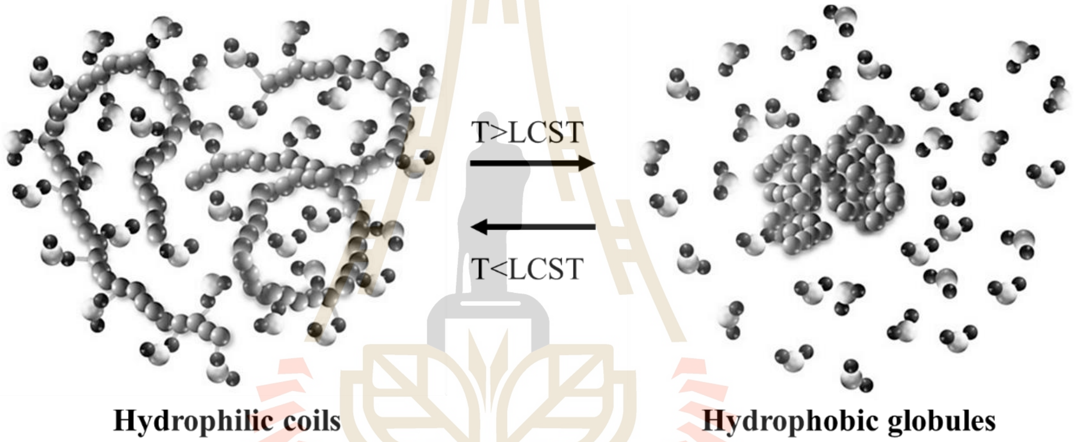


Figure 2.2 Coil to globule transition of a thermo-responsive polymer in aqueous solution (Weber, Hoogenboom, & Schubert, 2012)

2.2 The study of synthesis of PNIPAm grafted on various membranes

In order to prepare PNIPAm grafted membranes, several grafting methods, both chemical and physical, have been developed. For the chemical grafting techniques, UV-induced grafting, plasma-induced grafting and atom-transfer radical polymerization (ATRP) method have been used. The ATRP method is one of the most frequent used. This is because the technique has been shown to capable to initiate polymerization for a wide range of monomers. There are three steps in the fabrication of the gating membranes via the ATRP method, including hydroxylation, acylation, and grafting. All the steps require several chemicals. As a result, this technique produce several chemical waste including formaldehyde, dichloromethane, triethylamine, bromoisobutyryl bromide (BIBB), copper bromide ($CuBr_2$), and *N*,*N*,*N′*,*N″*,*N″*-Pentamethyldiethylene-triamine (PMDTA). They are toxic and hazardous as compared to UV-induced grafting and plasma-induced grafting method.

UV-induced graft polymerization is a proper method for the surface modification of biomaterials. It is a simple method and low cost. However, many factors are required in this method. The absorption intensity, radiation distance, wavelength and the usual factors such as degassing, substrate, initiators and sensitizers contribute to the ultraviolet radiation. Moreover, the solvent selection is very important. The effect of solvent may cause homopolymerization or grafting. The sensitivity to the UV radiation (choromophore) and rapid evaporation during the process can be observed from using acetone as a solvent, and because of those problems, the grafting amount is reduced (Biazar, Khorasani, & Joupari, 2013).

Plasma surface modification is one of the techniques that is useful for polymer grafting. In general, plasma contains ions, excited molecules, and energetic photons which can induce graft polymerization which called plasma-induced graft polymerization (PIGP) technique (Ohashi, Chi, Kuroki, & Yamaguchi, 2016). Among the many irradiation methods, vacuum plasma treatment has been widely used because of its commercial advantages. It offers flexibility, effectiveness, safety, and environmental friendliness. The vacuum plasma is effective at near-ambient temperature without damage to most heat-sensitive biomaterials. Plasma treatment modifies only the near surface of treated substrates and does not change the bulk material properties. It can be used to modify any kind of substrate geometry. Despite its advantages, costs associated with maintaining a vacuum and the constraint of batch processing have limited the acceptance of this technique. In contrast, atmospheric plasmas maintain the positive aspects of vacuum plasma treatment, without the limitations. Compared with conventional vacuum plasma treatment, atmospheric plasma treatment costs less and may be integrated into a continuous manufacturing process (Wang and McCord, 2007). For the general PIGP, the substrate was placed in a transparent glass tube. The glass tube was filled with argon gas and had been evacuated to a pressure of 10 Pa beforehand. The substrate was treated with a plasma at 10 W for 60 s. After that, the substrate was immersed in monomer solution immediately. Graft polymerization took place in a shaking temperature-controlled bath, set at 30°C, for a predetermined time. The technique has two successive steps. The first step is a plasma treatment to form free radicals on the substrate. The second step is grafting and polymerizing monomer with the radicals. Graft polymerization takes place in the substrate pores. The pores are filled with grafted polymer from the early stage of the polymerization. This also suggested that the monomer diffusion rate is much higher than the polymerization rate. As a consequence, graft polymerization can take place in the pores of the substrate (Yamaguchi, Nakao, & Kimura, 1991). In addition, due to the filling polymer is cooperated with the porous substrate by chemical bonds in this technique, it can prevent leakage at the interface between the pore wall and the filling polymer.

A modified version of PIGP was proposed by Suzuki, Kishida, Iwata, and Ikada (1986). According to this method, the plasma-irradiated substrate was exposed to contact with air for several minutes prior to the polymerization. During the air exposure, the free radicals on the substrate which obtained from plasma irradiation convert to peroxides. Unlike free radicals, which rapidly decay after irradiation, peroxides are comparatively stable and thereby minimize procedure variations. This method is also applicable to the preparation of pore-filling membranes. The grafting temperature is normally higher than 60°C to ensure the decomposition of peroxides, thereby initiating the polymerization (Xueqin, Hidenori, & Takeo, 2014). Only some radicals can react with monomers to grow the grafting polymer. The rest cannot react with monomers because of a hindrance effect of the grafted chains. As a result, this reaction rate was controlled by the diffusion rate of monomer through the pores. The grafting process includes steps : diffusion of monomer through the pores and then reaction of grafted polymer from the radicals. The balance between the two steps determine the location of grafted polymer in the substrate. Varying the monomer solvent composition could affected the graft polymerization rate by changing the monomer diffusivity relative to the reactivity. Thus, the grafted polymer location in the substrate could be controlled by changing the monomer solvent for the graft polymerization (Takeo, Shin-Ichi, & Shoji, 1996). Plasma-induced graft polymerization has a low energy consumption and high efficiency in producing initiators on the polymer surface while maintaining the bulk properties of polymer substrates including mechanical strength.

Lee and Shim (1997) synthesized *N*-isopropylacrylamide (NIPAm) grafted onto the porous polyamide membrane (127 μm thickness and 0.45 μm pore size) by plasma polymerization technique. The porous polyamide membrane was argon plasma reated using 50 mTorr and 30 W for 30 s. The sample was immediately exposed in the air then immersed in the 20 wt% NIPAm solution. The graft polymerization was carried out at 60°C for 2 h. The grafting yield was 202 μg cm^{-2}. X-ray photoelectron spectroscopy

(XPS) results of the poly(amide-*g*-NIPAm) surface showed a new peak ~288.0 eV as O=C-N. Fourier transform infrared attenuated total reflection (FTIR-ATR) spectra showed two methyl groups in isopropyl bond at 1370 cm^{-1}. These indicated that the NIPAm groups were grafted on the polyamide surface.

Yamaguchi, Ito, Sato, Shinbo, and Nakao (1999) developed a fast response molecular recognition ion gating membrane using linear PNIPAm with a crown ether receptor. Porous polyethylene (HDPE) film (thickness of 110 µm and pore size of 0.2 µm) was used as a porous substrate. The modified method of PIGP was used to fix a linear NIPAm-benzo-18-crown-6-acrylamide (BCAm) copolymer on the pore surface. The plasma-treated substrate was exposed to the air for 60 min, before immersed in monomer solution at 80°C. The water solution was emulsified with 4 wt% sodium dodecyl sulfate (SDS). NIPAm-BCAm grafted copolymer was filled inside the substrate as was observed by FT-IR mapping spectrum (step size 10 µm). Because monomers can diffuse from both surfaces, as a result both sides of the surface have a high graft amount. The response time for pore opening or closing was very short (within 30 s). In contrast, the response time of cross-linked thermosensitive gels was more than 10 min or hours.

Choi, Yamaguchi, and Nakao (2000) investigated thermosensitive membranes for macromolecular separation. Porous polypropylene (PP) film, with a thickness of 25 µm and a pore size of 0.25 × 0.075 µm, was used as the porous substrate. PP-*g*-NIPAm membranes with a grafted amount of 0.03-0.45 mg/cm^2 were obtained from a plasma-graft-filling polymerization. This method was similar to PIGP except for grafting temperature used was at 60°C. The grafting rate with a methanol aqueous solution was lower than that with a water solvent. The FT-IR peak ratio of amide II (derived from

NIPAm) at 1550 cm^{-1} to the methylene group (from PP) at 1450 cm^{-1} was obtained across the membrane cross section. The FT-IR peak ratio was evaluated the grafting profile of the membrane. The results showed that using a methanol/water mixture as the solvent, a homogeneous grafting formation throughout the thickness of the membrane was obtained. When water was used as a solvent, an asymmetric grafting formation exhibited. The grafted amount at the surface was greater than that in the center. Therefore, increasing the methanol concentration led to a decreasing reactivity relative to the monomer diffusivity. The total surface area of the membrane from BET method decreased with an increase in the grafting amount. Nonionic surfactant was adsorbed on the pore surface at 39°C and desorbed at 14°C. The pore surface of membrane changed between hydrophilic and hydrophobic in response to a stepwise temperature change between above and below LCST of PNIPAm.

Liang, Shi, Viswanathan, Peurrung, and Young (2000) prepared PNIPAm grafted polypropylene (PP) membranes by plasma polymerization. The PP microfiltration membrane with a thickness of 100 μm and a pore diameter of 0.2 μm was used in this study. The plasma of the PP membrane was carried out in a plasma reactor under 65 mTorr. Then, a 100 W nitrogen plasma was used for 5 min. The treated PP membrane was exposed immediately to the air and dipped into monomer solution. To initiate polymerization, the solution was heated to 100°C at the rate of 10°C/min. FTIR-ATR spectra can be confirmed that PNIPAm was formed on the surface of the PP membrane. SEM micrographs showed that both the increase of polymerization time and the concentration of NIPAm increased the grafting thickness and yield. The contact angle of the grafted PP membrane can be varied from 40° (at 20°C) to 90° (at 40°C). A rapid change of the advancing contact angle occurred around 34°C. The water fluxes at 42°C were 68 and 6.8 times higher than those at 20°C when the pressure drop was 13.6 and 27.0 atm, respectively. The increase of pressure drops retarded the transition of polymer chains. As a result, the change range of the water flux reduced.

Ito, Hioki, Yamaguchi, Shinbo, Nakao, and Kimura (2002) fabricated a molecular recognition ion gating membrane. The membrane was prepared by plasma graft copolymerization. The porous polyethylene (PE) film was treated with an argon plasma. After that, plasma activation method and a peroxide radical method were used for grafting. In case of the plasma activation method, the substrate was immediately immersed in monomer solution. Then, the membrane was heated to 60°C. In case of the peroxide radical method, the plasma-treated substrate was in contact with air for 60 s. After that, the substrate was immersed in monomer solution. Then, the membrane was heated to 80°C. The free radicals from plasma reacted with O_2 and converted into peroxide radicals. The degree of grafting was between 0.3 and 0.5 mg/cm^2. FT-IR spectra showed the copolymer ratio of acrylamide and methylacrylate. This ratio was estimated from the ratio of the peak height. The result showed that the ratio in the grafted copolymer by the peroxide radical method was higher than by the plasma activation method.

Chu, Niitsuma, Yamaguchi, and Nakao (2003) prepared the PE-*g*-PNIPAm membranes using a plasma-graft pore-filling polymerization method. PIGP method was employed to graft the linear PNIPAm chains into the substrates. The PE H2100 substrate (a thickness of 100 μm, a porosity of 69%, and a pore size of 0.28 μm) was used for grafting. They applied power 30 W for plasma treatment and the grafting time were 56-1,282 min. Degree of grafting were 1.41 and 6.06 mg/cm^2 for 1 and 5 wt% of NIPAm concentration, respectively. A typical IR-mapping spectrum across the membrane thickness (step size 10 μm) showed the PNIPAm peaks exist throughout the entire membrane thickness. The FT-IR absorbance ratio of the amide II peak to the PE peak was found to be directly proportional to the graft yield of PNIPAm. This indicated that the grafted polymer formed homogeneously in the pores of the membranes. These results were confirmed by correspondence of the calculated pore sizes and the measured values from mercury intrusion method. The hydraulic permeability experiments were carried out with trans-membrane pressure 50 kPa. The temperature of the water was kept constant at 25°C or 40°C using a thermostatic unit. At 25°C, the water flux decreased rapidly with increasing the PNIPAm graft yield. At 40°C, the hydrophobicity of the inside pore surfaces increased with shrinking state of PNIPAm. Owing to the stronger hydrophobicity, lower frictional drag force was resulted for the water flowing through the membrane. Hence, at low graft yield, the water flux of PNIPAm-*g*-PE membrane at 40°C was larger than that of the ungrafted membrane. The graft yield in the range 0.4-0.8 mg cm^{-2} was suggested for the effective thermo-responsive membrane. The diffusional permeability experiments were carried out using a standard side-by-side diffusion cell. The diffusion cell was located in a constant-temperature incubator. Each test membrane was immersed in the carbazochrome sodium sulfonate (CCSS) solution overnight before starting the experiments. When the graft yield was low, the diffusional coefficient of solute across the membrane was higher at temperature above the LCST than that below the LCST. Owing to the pores were controlled open/close by the shrinking/swelling mechanism of PNIPAm. When the graft yield was high, the diffusional coefficient at temperature above the LCST was lower than that below the LCST. This is due to high impact of hydrophobic PNIPAm gates at above the LCST, the solute hardly diffused through the PNIPAm gates.

Li, Yan, Chu, Zhu, Wang, Xia, and Chen (2004) prepared poly(*N*-isopropylacrylamide) (PNIPAm) grafted onto porous poly (vinylidene fluoride) (PVDF) membrane substrates. Porous PVDF membranes, with a pore size of 0.22 µm and a thickness of 62.5 µm, were used as the flat porous membrane substrates. Plasma-induced pore-filling polymerization method was employed to graft the linear PNIPAm chains into the pores of the flat membrane. The plasma treatment time was 60 s, the reaction atmosphere was argon gas, the pressure was 10 Pa, and the grafting temperature was 30°C. The plasma power was changed from 10 to 30 W. The NIPAm concentrations in the monomer solutions were 1 and 3 wt%, respectively. The grafting time was from 60 to 240 min. The results showed that with an increase in the plasma power, the monomer concentration, or the grafting time, the graft yield of PNIPAm on the membrane increased. The diffusional permeability experiments of membranes were carried out using a standard side-by-side diffusion cell. The solute was sodium chloride. The concentration of NaCl was determined by measuring the electrical conductance with an electrical conductivity meter. Both the hydraulic permeability and the diffusional permeability through the PVDF-*g*-PNIPAm membranes were strongly dependent on the PNIPAm grafting yield. With an increase in the grafting yield, the hydraulic permeability (water flux) decreased rapidly at both 25 and 40°C because of the decrease of the pore size. The diffusional permeability of the solute across the membranes also changed dramatically at temperatures around the LCST of PNIPAm. When the grafting yield was low, the diffusional coefficient of the solute across the membrane was higher at temperatures above the LCST than that below the LCST, owing to the pores of the membrane being controlled open/closed by the shrinking/swelling mechanism of the grafted PNIPAm gates, while when the grafting yield was high, the diffusional coefficient was lower at temperatures above the LCST than that below the LCST, owing to the hydrophilic/hydrophobic phase transition of the grafted PNIPAm gates.

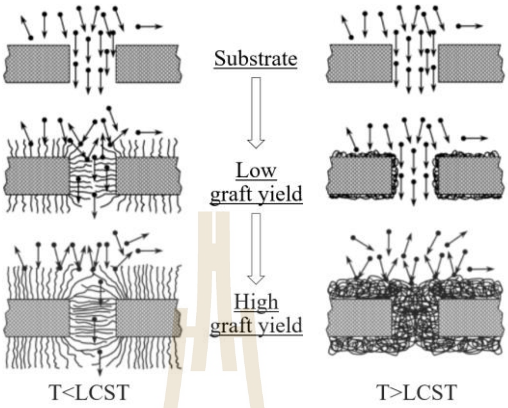


Figure 2.3 Schematic illustration of thermo-responsive diffusional permeability through PNIPAm grafted membranes with different grafting yields (Li et al., 2004)

Xie, Chu, Chen, Xiao, Wang, and Qu (2005) investigated microstructure of PNIPAm grafted polycarbonate track-etched (PCTE) membranes. Porous PCTE membrane with an average pore size of 200 nm and a thickness of 10 μm was used as the substrates. PIGP was employed to graft linear PNIPAM chains on the surface and into the pores. The NIPAm concentrations in the monomer solutions were from 1 to 5 wt%. The polymerization time was from 2 to 6 h. XPS and FT-IR were used to confirm that the PNIPAm was successfully grafted on the porous PCTE substrates. The morphologies from SEM showed uniform pore geometry, cylindrical, and straight pores of the ungrafted membranes. The grafted PNIPAm polymers were formed inside the pores throughout the entire membrane thickness. There was not a dense PNIPAm layer formed on the membrane surface even at a pore-filling ratio as high as 76.1%. Pore-filling ratio (F) is defined as volume of grafted PNIPAm polymer in the pore (cm^3) divided by volume of the pore before grafting PNIPAm (cm^3). With the pore-filling ratio increasing, the pore diameters of PNIPAm grafted membranes became smaller. At the temperatures above the LCST of PNIPAm in this study, the critical pore-filling ratio for choking the pores of membranes in water was in the range from 30 to 40%. AFM images showed the pores with high pore-filling ratio (e.g., 67.0%), might be blocked by the grafted PNIPAm polymer in the pores but not near the surface.

Yang, Chu, Li, Zhao, Song, and Chen (2006) studied the effect of the substrate properties on the thermo-responsive gating characteristics of the PNIPAm grafted membranes. The hydrophilic Nylon-6 and hydrophobic poly(vinylidene fluoride) (PVDF) porous membrane (average pore size of 0.22 μm) were used as substrates and compared. Plasma-graft pore-filling polymerization was employed to graft the linear PNIPAm chains to the membrane substrates, like PIGP but applied power 30 W for plasma treatment. The NIPAm concentrations in the monomer solutions were from 1-3 wt% and the polymerization time was varied from 60-240 min. SEM micrographs indicated that PNIPAm could be grafted on both the outer surface and the inner surfaces of both substrates, although the microstructures of the porous substrates were different. The optimum grafting yield of PNIPAm for the PNIPAm-*g*-Nylon-6 membranes, corresponding to the largest thermo-responsive gating coefficient was 7.47%, while that for the PNIPAm-*g*-PVDF membranes was just 2.81%. The effect of differences in the microstructure of the porous substrates, Nylon membranes honeycombed porous structure and PVDF membranes were finger-like pores with a thin functional top layer, and differences in the hydrophilicity of the porous substrates could be explained the above results.

Wang and McCord (2007) investigated atmospheric plasma treatment with subsequent graft copolymerization was used to graft PNIPAm onto nylon and polystyrene (PS) surfaces. Nylon 6,6 film and 60-mm nontissue culture-treated polystyrene (PS) plates were used as the substrates. In this investigation, PS and nylon were treated for 1 min in the batch chamber with atmospheric plasma generated from 100% He. The distance between sample and electrode was 1 in. The power level used was 4.8 kW. The frequency was 5 kHz. The flow rate of He was 10.18 L/min. After He plasma treatment, the samples were immediately immersed into a NIPAM aqueous solution (5% wt) in a reaction kettle. The kettle was then sealed under N_2 and placed in a 60°C shaking water bath to begin the graft copolymerization for 24 h. The atmospheric plasma treatment activates the substrate surface and forms free radicals on the substrate surface. Since the plasma chamber is not sealed, there is always oxygen in the system, and the free radicals react with oxygen to form hydrogen peroxide groups either inside the chamber during plasma treatment or upon removal and exposure to the ambient environment. The hydrogen peroxide groups are thermally labile in nature and initiate the graft copolymerization of NIPAm to introduce graft brush layers on the surface (Figure 2.4). FTIR spectra confirmed the grafting of PNIPAm on the PS and nylon surfaces. The graft yield for nylon is 20 times higher than that for PS. This is due to their different chemical structures. Nylon has many N-H and C=O bonds, which are more susceptible to chain scission and free radical formation under atmospheric plasma. The addition of Mohr's salt $[Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O]$ suppressed the homo-polymerization and enhanced graft copolymerization. The graft yield for PS increased from 0.056 to 0.087 mg/cm^2, and graft yield for nylon increased from 1.67 to 1.93 mg/cm^2.

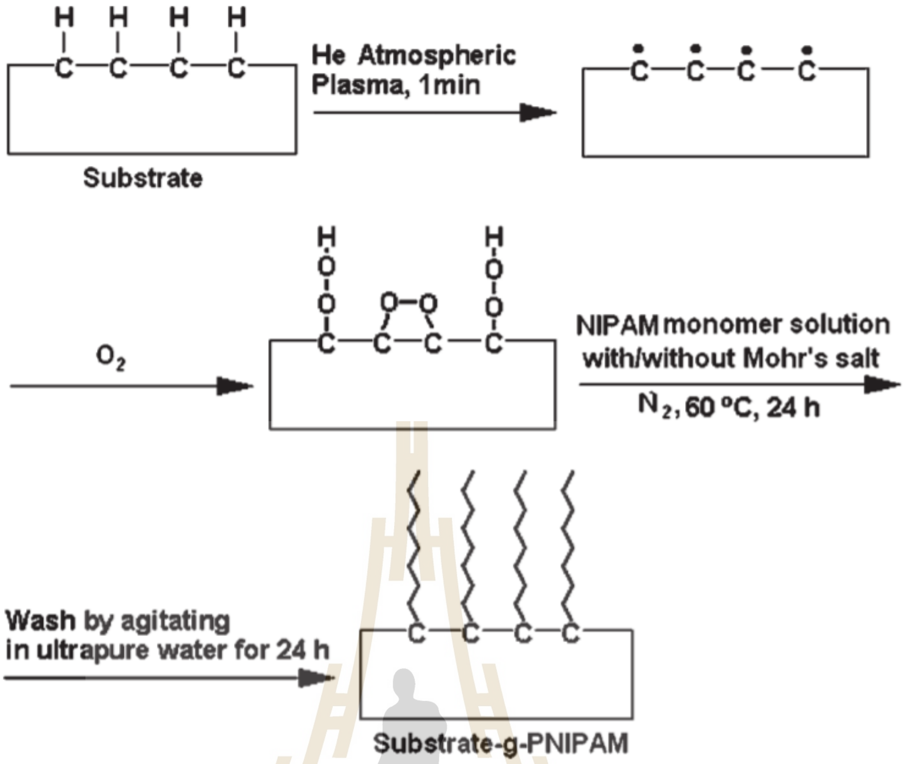


Figure 2.4 The schematic of graft copolymerization of NIPAm on PS and nylon surfaces (Wang and McCord, 2007)

Xie, Li, and Chu (2007) investigated the adjustment of response temperature of thermo-responsive membranes. Hydrophilic or hydrophobic monomers were added into NIPAm solution for fabrication of thermo-responsive gates for the membranes. Both porous polyvinylidene fluoride (PVDF) and Nylon-6 (N6) membranes, with an average pore size of 0.22 μm, were used as the porous membrane substrates. PNIPAm-based gates were grafted on the porous substrates by PIGP. Poly(*N*-isopropylacrylamide-*co*-acrylamide) (PNA) gates were grafted onto PVDF substrates. Poly(*N*-isopropylacrylamide-*co*-butyl methacrylate) (PNB) gates were grafted onto N6 substrates. The polymerization time was in the range of 30-60 min for preparing PNA-*g*-PVDF membranes and 60-120 min for fabricating PNB-*g*-Nylon membranes. XPS C_{1s} and O_{1s}

core-level spectra from X-ray photoelectron spectroscopy (XPS) was used to show successful grafting. A new peak emerged at binding energy of 286.110 eV (C atom of C-N) in the C_{1s} spectrum of the PNA-*g*-PVDF membrane. A new peak also emerged at binding energy of 531.656 eV in the O_{1s} spectrum of PNA-*g*-PVDF membrane (for the O atom of C=O double bond). While there is no peak in O_{1s} spectrum of ungrafted membrane. A new peak emerged at binding energy of 533.200 eV in the O_{1s} spectra of PNB-*g*-Nylon. The water flux through the membranes showed shifting of the temperature range of dramatic change of water flux through the grafted membranes. This is due to hydrophilic or hydrophobic monomer changed the content of donators of hydrogen bond. Therefore, the response temperatures of the grafted gating membranes could be increased with increasing the molar ratio of hydrophilic monomer. Also, an increase in the molar ratio of hydrophobic monomer resulted in a decrease of the response temperatures.

Chen, Xie, Yang, Li, Zhu, and Chu (2009) compared gating characteristics of thermo-responsive membranes with grafted linear and crosslinked PNIPAm gates. Porous nylon-6 (N6) membrane with the average pore size of 0.22 µm and thickness of 96 µm was used as a substrate. PIGP was employed to graft linear and crosslinked PNIPAm gates onto N6 membrane substrates with 0.5 wt% NIPAm in the monomer solution. *N*,*N*’-Methylenebisacrylamide (MBA) was added into the NIPAm monomer solution (NIPAm/MBA = 100:1 (molar ratio)) as the crosslinker. The grafting temperatures were chosen as 25°C and 40°C, which are below and above the LCST of PNIPAm, respectively. The grafting temperature influenced homogeneous grafted layer throughout the pore length. When the operation pressure increased to 0.14 MPa, the water fluxes at 25°C were measured. The water flux of the linear PNIPAm grafted membranes, which prepared at 25°C abruptly increased from 0 to 0.0017 mL cm^{-2} s^{-1}. This is due to the flexibility of the linear grafted PNIPAm chains in the membrane pores. The crosslinked network structure of the grafted PNIPAm was mechanically stronger than the linear chain structure under high operation pressure. On the other hand, the thickness of the grafted layer in the crosslinked PNIPAm grafted membrane was slightly thinner than that in the linear PNIPAm grafted membrane. As a result, the flux of water through the crosslinked PNIPAm grafted membrane was larger than that through the linear PNIPAm grafted membrane under the same operation pressure. The thermo-responsive gating coefficients under different operation pressures remain unchanged when each operation pressure is higher than a certain critical pressure value. The thermo-responsive gating coefficient of the linear PNIPAm grafted membrane, which prepared at 25°C was the highest among the four kinds of grafted membranes. Both linear PNIPAm grafted at 40°C and crosslinked PNIPAm grafted at 25°C membranes exhibited stable and repeatable thermo-responsive gating characteristics under operation pressure of 0.26 MPa.

Smolinska and Bryjak (2012) synthesized PNIPAm chains grafted on microporous polypropylene membranes with plasma treatment and UV radiation. Microporous PP membrane (Celgard 2500, thickness of 25.4 μm, pore size of 0.05-0.20 μm, and porosity of 45%) was placed into the plasma reactor and treated with argon flow 60 L/h at voltage 20 kV and current 5 mA for 60 s. After that, the samples were allowed to stay in the air for 10 min and then they were immersed in 20 vol% monomer concentration. The solution was irradiated by UV radiation for 7 min. FTIR spectroscopy used to confirm that membranes were grafted successfully. The peaks at 1540 cm^{-1} and 1650 cm^{-1}, attributed to C=O and N-H groups of PNIPAm. The thermo-responsive gating characteristic could be measured from water flux at 20°C and at 43°C. When temperature was decreased from 43°C to 20°C, water flux dropped from 25 L/m^2 h down to 2 L/m^2 h. However, the grafting yield of this study no larger than 0.125 mg/cm^2.

Xueqin, Hidenori, and Takeo (2014) found an approach to induce PIGP at the lower temperature range from 25 to 40°C. Normally, the peroxides being the assumed initiator, the applied grafting temperature is higher than 60°C to assure the decomposition of peroxides, thereby initiating the polymerization. In this study, high-density grafting of 2-acrylamido-2-methylpropane sulfonic acid on porous polyethylene membrane can be achieved by incorporating an infiltration agent under acidic condition. Porous HDPE membranes (thickness 27mm, porosity 50%, maximum pore size 150 nm) were used as the porous substrate. The infiltration agent SDS facilitated the infiltration process, ensuring the distribution of the AMPS monomers to the active sites inside the pores of HDPE membranes. Moreover, the pH of monomer solution was affected on the initiation process of PIGP. Under suitable acidic conditions, the polymerization proceeded at temperatures as low as 25°C even after all residual radicals in the membranes had decayed. In addition to the hydroperoxides, some radicals may survive after the exposure to air (residual radicals). Unlike hydroperoxides, which require heat to reach an active state, the residual radicals have high-chemical reactivity at room temperature and can initiate the polymerization directly. Nevertheless, HDPE-*g*-poly-AMPS membranes with required grafting yield were achieved easily by modulating the grafting time. The mild thermal conditions allow maintenance of the bulk property of the substrates. Comparing the plasma-treated substrates treated with different infiltration agents prior to polymerization, grafting amount about 600 μg/cm^2 were obtained when using 10 wt% SDS and ethanol. They can both help the monomer solution overcome the huge interface tension and thus infiltrate into the pores of the substrate.

Ohashi, Chi, Kuroki, and Yamaguchi (2016) studied the relationship between the permeable properties and the structural properties of PNIPAm-*g*-PC membranes. The grafted membrane was prepared using the PIGP technique-peroxide method. The degree of grafting was evaluated by the filling ratio. The grafting temperature were 40 and 80°C. The results showed that filling ratio and grafting rate at 40°C were higher than at 80°C. However, the grafting density at 80°C was higher than at 40°C. Due to peroxide decomposition rate is faster at higher temperature. The consumption of initiators is faster and the resultant grafting polymer becomes more crowded at 80°C. The filling ratio between 10% and 20% were reported to exhibit clear pore open/close functionality. Thus, the filling ratio of approximately 12% was chosen to compare gating performance. When the grafted PNIPAm was in the swollen state. The PC-*g*-PNIPAm membrane fabricated at 40°C exhibited a larger permeability than that fabricated at 80°C. Due to a larger grafting density provided less space between polymer chains near the pore surface, resulting in a better pore-close performance. When the grafted PNIPAm was in the shrunken state. The PC-*g*-PNIPAm membrane fabricated at 40°C exhibited a smaller permeability than the membrane fabricated at 80°C. Because of its low grafting density, the structure of the polymer layer, especially near the pore surface, seemed to be loose. This provided more space between the polymer chains for water permeation. Hence, PC-*g*-PNIPAm membrane fabricated at 40°C led a worse pore-open performance.

2.3 The study of microwave-assisted preparation for PNIPAm grafted membrane

In the past few years using of microwave irradiation has become a well-established technique to promote and enhance chemical reactions. Microwave irradiation is electromagnetic irradiation in the frequency range of 0.3 to 300 GHz. All domestic microwave ovens and all dedicated microwave reactors for chemical synthesis operate at a frequency of 2.45 GHz. The energy of the microwave photon in this frequency region (0.0016 eV) is too low to break chemical bonds. It is also lower than the energy of Brownian motion. Therefore, it is clear that microwaves cannot induce chemical reactions (Gabriel et al., 1998). Microwave-enhanced chemistry is based on the efficient heating of materials. Microwave-assisted heating is different from conventional (conductive) heating. The dielectric character of microwaves provides non-contact heating. This phenomenon is dependent on the ability of a specific material (solvent or reagent) to absorb microwave energy and convert it into heat. The electric component of an electromagnetic field causes heating by two main mechanisms. They are dipolar polarization and ionic conduction. Irradiation of the sample at microwave frequencies results in the dipoles or ions aligning in the applied electric field. In the process, energy is lost in the form of heat through molecular friction and dielectric loss. The amount of heat generated by this process is directly related to the ability of the matrix to align itself with the frequency of the applied field. The heating characteristics of a particular material (for example, a solvent) under microwave irradiation conditions are dependent on its dielectric properties. The main advantages of microwave heating are a strong reduction in reaction time and a high potential to contribute to green and sustainable chemistry (Oliver, 2004).

2.3.1 Principle of microwave heating

Microwaves are in the region of the electromagnetic spectrum and classified as nonionizing energy. Nonionizing energies can act at the molecular level and thus are unable to change the constitution of substances. In general, materials can transmit, reflect, and absorb microwaves. For metals, microwaves do not affect the material and are reflected by its surface. They are normally excellent reflectors, and they are not heated by microwaves. Transparent materials can transmit microwaves without considerable effects. Absorption occurs when the material partially or completely absorbs the microwaves. For liquids, dipolar rapid rotation is promoted causing the heating of the material (Figure 2.5). As each molecule is responsible for heating. The dissipation of heat is considered uniform and localized, in contrast to conventional heating. Energy in conventional heating is transferred to the materials via heat conductive, convective, or radiative transfer. In this case, heat is transferred from the heating source through the vessel wall into the content in the vessel (Figure 2.6).

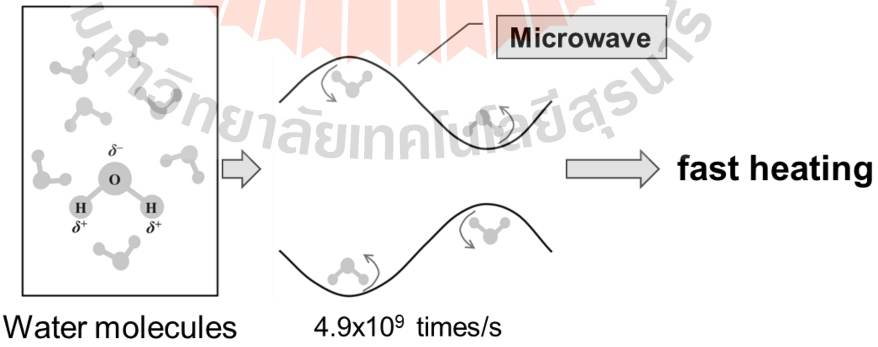


Figure 2.5 Schematic representation of the alternating alignment of water molecules under the oscillating electric field induced by microwaves (Mello, Barin, & Guarnieri, 2014)

(a) (b)

Figure 2.6 Schematic representation of heating : (a) Conventional heating and (b) Microwave heating

2.3.2 Microwave-assisted polymerization

Shi and Liu (2006) prepared PNIPAm-based hydrogels by microwave irradiation. Poly(ethylene oxide)-600 (PEO-600) was chosen as reaction medium and microwave-absorbing agent. The microwave-assisted polymerization/crosslinking reaction was performed in a microwave oven of Panasonic NN-K542WF with a 2450 MHz frequency. Microwave output power was modulated from 75 to 800 W for 15 min. Under 75 W, the temperature of the reaction mixture increased from 20 to 114°C within 3 min. Comparing with the reaction mixture incubated in oil bath, it taken nearly 14 min. The reaction mixtures start to form hydrogel networks at 56°C. The conventional heating taken 300 s to attain the temperature. The reaction systems under 340, 170, and 75 W microwave irradiation taken only about 10, 28, and 48 s respectively. The maximum yields (98 and 97%) obtained under 170 and 75 W microwave irradiation. FTIR spectra exhibited disappearance of NIPAm and BIS absorbing peaks. This indicated that the PNIPAm hydrogel was successfully synthesized in PEO-600 under microwave irradiation.

Ma, Cui, and Dong (2007) synthesized the Poly(2-acrylamide-2-methylpropane sulfonic acid (AMPS)/NIPAm) hydrogel. The polymerization between AMPS and NIPAm was initiated by the microwave low temperature plasma (MLTP). AMPS and NIPAm monomers were mixed with a certain proportion and then placed in the airtight chamber. After the system was degassed to 3 Pa, the monomers were vaporized till the gas pressure in the system rose spontaneously to 30 Pa. Subsequently, the MLTP of the mixed gases was generated at power of 80-250 W. The mixed monomers were exposed to the plasma for 60-360 s. The polymerization was carried out in the water bath at 30°C for 10h. MLTP treatment power and time are the two key factors to the MLTP-initiated polymerization. When the power increasing, the swelling ratio (SR) of P(AMPS/NIPAm) hydrogel increased rapidly. However, after the power was beyond 100 W, the SR decreased. When the treatment time was too short, the free radicals could not be induced. However, an overlong exposing time brought on excess actions of active particles, which made the SR decreasing due to the excessive crosslinking. The results showed that with the increase in treatment time, the SR increased first and then decreased after the time was beyond 120 s.

2.4 The study of oil-water emulsion separation for PNIPAm grafted membrane

With the environmental pollution accompanying the development of industry, separation of oil/water mixtures has been a worldwide problem. Hydrophilic or hydrophobic porous materials, capable of removing oil from oil-water emulsions, are extensively developed. As for oil strainer, it is usually created by the process of coating the porous substrates with hydrophobic substances. The smart membrane was found to be feasible to separate oil-water emulsion. Because the hydrophilicity and hydrophobicity of grafted membrane, oil-in-water and water-in-oil emulsion should separate by gravity force at different temperature.

Ou, Ranwen, Jing Wei, Lei Jiang, George Simon, and Huanting Wang (2015) fabricated a robust, thermoresponsive polymer membrane produced by the combination of an elastic polyurethane (TPU) microfiber web and poly(*N*-isopropylacrylamide) (PNIPAm). PNIPAm hydrogel was coated the on the TPU microfibers' surface by free-radical polymerization. After 2 h reaction at 70°C, TPU-PNIPAm membranes were obtained. The membrane was fixed between two glass tubes. At room temperature, the 1 wt% silicone oil-water emulsion was poured into the upper tube, and the separation was achieved by gravity only. The 99 wt% silicone oil-water emulsion was heated to 45°C. Then, it was poured into the separation setup in an oven set to 45°C to achieve separation. The TPU-PNIPAm membrane which was loaded 3.6 wt% PNIPAm hydrogel was able to exhibit excellent ability to separate oil-water emulsions. At room temperature, 1 wt% silicone oil-water emulsion was separated, and the separation efficiency was higher than 99.26%. At 45°C, 99 wt% silicone oil-water emulsion was separated, and the separation efficiency was 99.85%. The separation efficiencies were stable both at room temperature and 45°C. However, oil permeated through the membrane, but the permeation of oil was blocked when the membrane surface was covered by water at 45°C, and thus, both oil and water were retained.

2.5 The study of contact angle of PNIPAm grafted membrane

The wetting behavior of solid surfaces by a liquid is a very important aspect of surface chemistry, which may have a variety of practical applications. When a liquid droplet contacts a solid substrate, it will either remain as a droplet or spread out on the surface to form a thin liquid film, a property which is normally characterized using contact angle (CA) measurements. For a solid substrate, when the CA of water or oil on it is larger than 150°, it is called superhydrophobic or superoleophobic, respectively. On the other hand, when the CA of water or oil on a surface is almost 0°, it is called superhydrophilic or superoleophilic, respectively. On a PNIPAm-modified flat substrate, the CA could be switched between hydrophobicity and hydrophilicity as the temperature passed through the LCST, which is the result of the competition between intra- and intermolecular hydrogen bonding (Figure 2.7). When the polymer was modified on a rough surface, the wettability could be changed from 0° to 149.3° as the temperature was elevated from 25°C to 40°C, which indicates that reversible switching between superhydrophobicity and superhydrophilicity has been realized by thermal treatment (Feng & Jiang, 2006).

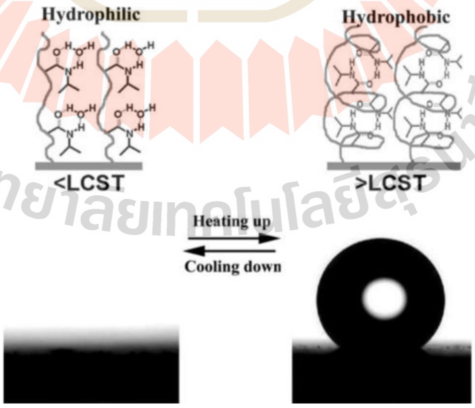


Figure 2.7 Schematic diagram of the molecular mechanism and water-drop profile of the temperature-responsive switching on a PNIPAm film (Feng & Jiang, 2006)

Ou, Ranwen, Jing Wei, Lei Jiang, George Simon, and Huanting Wang (2015) determined the contact angle of the swollen TPU-PNIPAm membrane using a contact angle goniometer (Dataphysics OCA15, Dataphysics, Germany). The average value was obtained from more than 5 measurements per sample. The results showed that the water contact angles of swollen TPU-PNIPAm membrane (7.6, 13.4, and 25.3 wt%) were low at room temperature and and increased at 45°C. This exhibited the TPU-PNIPAm membrane exhibited switchable superwettability. At room temperature, with increasing hydrogel loading, the contact angles of the membranes increased. Meanwhile the hydrogel filled the space between TPU microfibers. The membrane roughness decreased, resulting in a similar wettability to PNIPAm hydrogel. At 45°C, the contact angles initially increased and then decreased with increasing hydrogel loading. TPU membrane with 3.6 wt% PNIPAm loading reached the highest value. TPU-PNIPAm-3.6 membrane was superhydrophilic, with a water drop spreading in a time frame of less than 0.094 s, but became superhydrophobic (150.2°) at 45°C. Moreover, TPU-PNIPAm-3.6 submerged under water at room temperature, and floated on the surface of water without a water droplet on the membrane surface at 45°C.

CHAPTER III

EXPERIMENTAL

3.1 Materials

The Nylon membranes used as porous substrats in this study were acquired from Whatman Co. They possessed 0.2 µm of an average pore size and 150-187 µm in thickness. The main monomer and a crosslinker used were *N*-isopropylacrylamide (NIPAm) (98%) and *N*, *N'*-methylenebisacrylamide (BIS), respectively. They were purchased from TCI Co. and used without further purification. Deionized water was used in all experiment throughout the study.

3.2 Grafting of linear and crosslinked PNIPAm onto porous Nylon-6 substrates

3.2.1 Plasma peroxide method

The plasma treatment system was kindly granted the access and time slot to use for the grafting experiments by the Synchrotron Light Research Institute at Suranaree University of Technology. Pico reactor (Diener electronic, Germany) with 150 mm in chamber diameter and 320 mm in length was used at an operating frequency of 2.46 GHz. Pressure, power input, and carrier gas feed rate were kept constant at 10 Pa, 30 Watts, and 5 sccm (standard cubic centimeters per minute), respectively for 30 s in every experiment. The as-received Nylon membranes were treated with argon plasma on both sides. These treated membranes were then exposed to the atmospheric air for 2 days, so that the free radicals reacted with oxygen in the air and formed hydrogen peroxide groups on the surface of the membranes. To generate the free radicals on the Nylon surface for grafting, these parameters were kept constant.

Measurements of Amount of Radical

In order to verify and quantify the amount of the free raducals induced by argon plasma technique on the Nylon-6 membranes' surface, the following chemicals and procedure were used (Yamaguchi, Nakao, & Kimura, 1996).

Chemicals :

2,2-Diphenyl-1-picrylhydrazyl (DPPH) ($C_{18}H_{12}N_5O_6$, Sigma-Aldrich; St. Louis, USA) and Benzene (Loba-AR grade, Bombay)

Preparation :

The solution of 33.4 mg/L of 2,2-Diphenyl-1-picrylhydrazyl (DPPH) was prepared using 0.0033 g of DPPH which was dissolved in benzene and made up to 100 ml of final volume and stored at room temperature.

Procedure :

Nylon substrates were plasma treated with different conditions. When the radicals were exposed to the air, they interaced with O_2 and became peroxy radicals, and some of them became peroxides. The peroxide concentration profile was assessed using a method developed by Piao et al. which uses DPPH solution. The estimation of the peroxide concentration was made based on the half of the amount of DPPH reacted. The measument was carried out after the substrates were exposed to air for 2 days, these substrates were then placed in DPPH solution which held at 70°C for 15 hours. This step turned peroxide groups to peroxy radicals. The amount of peroxide formed in each substrate was quantified by using UV-VIS which measured the disappearance of DPPH.

3.2.2 Microwave-assisted polymerization

NIPAm monomer was grafted onto the surface of Nylon-6 membrane using microwave-assisted polymerization. In order to do so, the plasma treated membranes were submerged in NIPAm monomer solution and then irradiated with microwave. The heat genterated by the microwave irradiation induced the grafting polymerization. The grafting mechanism for PNIPAm onto nylon porous membrane surfaces is schematically portrayed as shown in Figure 3.1. Normally, when the peroxides being the assumed initiator, the temperature applied for grafting is higher than 60°C. The high temperature was to guarantee the decomposition of peroxides which yielded alkoxy radicals in aqueous solution, thereby initiating the polymerization (Xueqin et al., 2014).

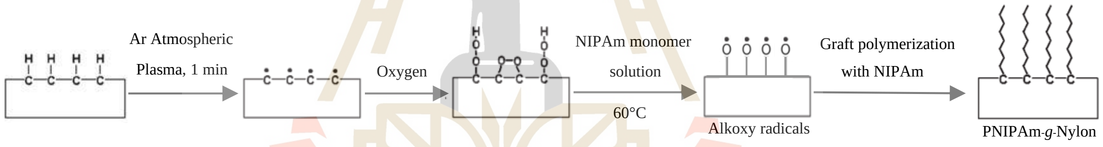


Figure 3.1 Grafting mechanism of NIPAm onto Nylon-6 porous membrane's surface using plasma peroxide method coupled with microwave-assisted polymerization (Katesripongsa and Trongsatitkul, 2019)

Microwave-assisted polymerization was carried out in a commercial microwave oven (Samsung MS23K3513AW) with a frequency of 2.45 GHz and output power of 100-800 W. Nylon membrane was irradiated by microwave for 5, 10, and 15 min. Effects of microwave irradiation output power, irradiation time, the presence/absence of crosslinker, and concentration of the NIPAm monomer on grafting yield and structure were studied. It was expected to obtain the optimum condition for grafting of PNIPAm onto the porous Nylon membrane. The optimization of microwave-assisted polymerization step was carried out as followed.

1. To study the effects of microwave irradiation output power and time on grafting yield, the monomer solution comprised of a constant concentration of 10 wt% NIPAm in water was used. The process started with a Plasma treated membrane was completely submerged under the monomer solution in a Petri dish. Then the membrane along with the monomer solution in the Petri disch was placed on the microwave oven for microwave irradiation. The irradiation of microwave power and time were varied from 100 to 800 W and 5 to 15 min, respectively. After microwave irradiation step ended, the grafted membrane was repeatedly rinsed with DI water. It was then, mildly sonicated in a shaking water bath (WNB29, Memmert) at 30°C for 12 h to ensure the removal of any residual chemicals. Finally, the grafted membrane was dried at 50°C for 12 h in an oven (VD53, Binder) before being tested or characterized.

2. The study of the effects of the presence of BIS crosslinker and the monomer solution concentration were performed by using the optimum condition of microwave irradiation obtained from the prior step. The monomer solutions, with and without crosslinker, with a constant solid content were prepared. In the case of the solution with the presence of crosslinker, the constant weight ratio of 800:50 (NIPAm:BIS) was used (Shi & Liu, 2006). The concentrations of monomer solution varied from 2 to 10 wt% were prepared. The grafting of the treated membranes with the different monomer concentrations was carried out as described above. Different conditions used in this study were summarized in Table 3.1.

The overview of the experiment is shown in Figure 3.2.

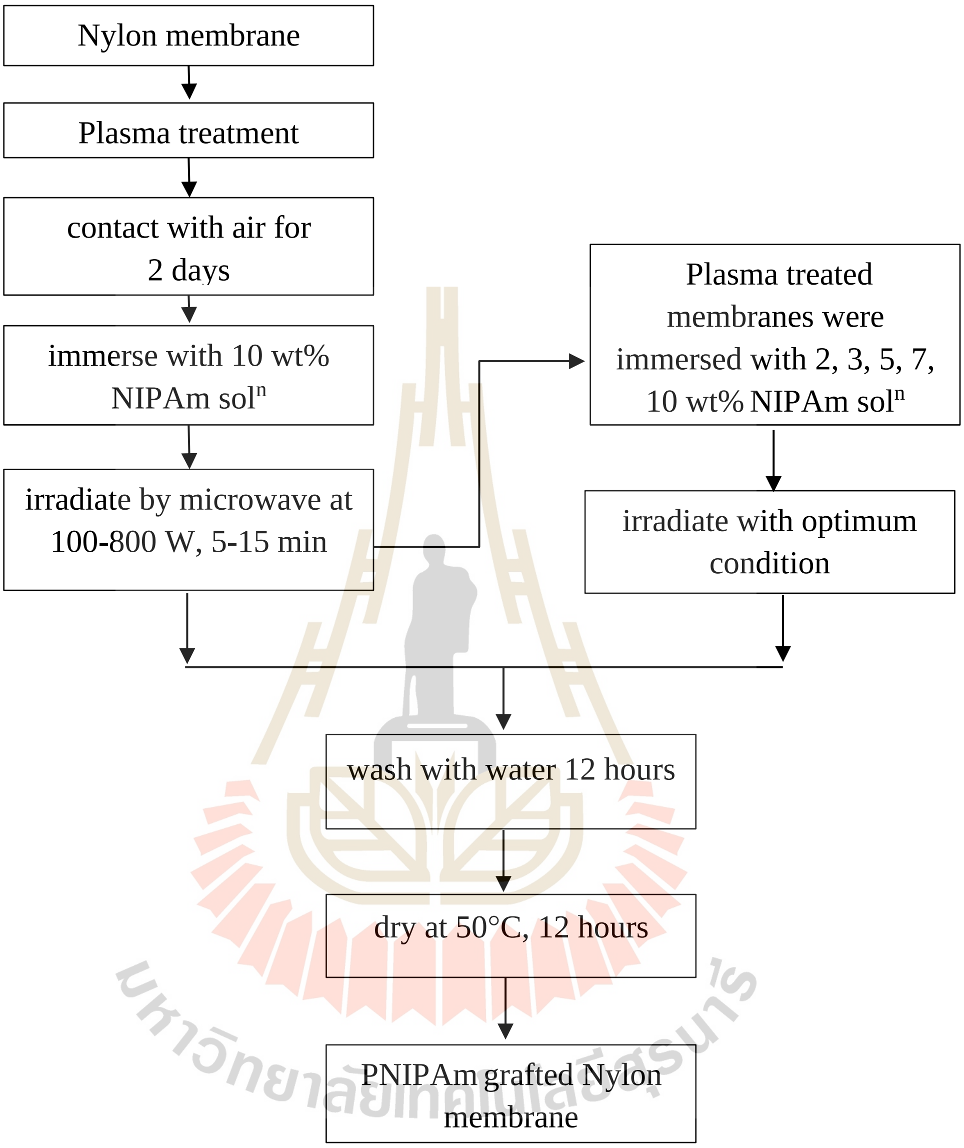


Figure 3.2 The overview of preparing PNIPAm grafted Nylon membrane

Table 3.1 Conditions for grafting the PNIPAm grafted Nylon membranes.

Condition no.	NIPAm (wt%)	Output power (W)	Irradiation time (min)
1	10	100	5
2			10
3			15
4		450	5
5			10
6			15
7		800	5
8			10
9			15
10	7	Optimum condition	
11	5		
12	3		
13	2		

3.3 Characterization of Membrane

The grafted membranes prepared using different compositions and conditions were characterized via FTIR, SEM, and weighing method for the proof of reaction, change in structure, and grafting yield, respectively.

3.3.1 Grafting yield

The grafting yield of the grafted membrane may be defined as the mass increase ratio after grafting PNIPAm. Equation used for calculation of grafting yield is as shown below (Yang et al., 2006).

$$Y = \frac{W_g - W_0}{W_0} \times 100\% \tag{3.1}$$

where Y is the grafting yield of PNIPAm on the membrane substrate, and W_g and W_0 are the mass of the membrane after and before grafting, respectively.

3.3.2 FTIR analysis

Fourier Transform Infrared Spectrometer (FT-IR) (Tensor 27, Bruker, Billerica, MA, USA) with an attenuated total reflection (ATR) mode was used to confirm the grafting of PNIPAm polymer onto the Nylon 6 porous membranes. The spectra were collected at 4 cm^{-1} resolution with over 64 scans.

3.3.3 Morphological analysis

Scanning electron microscopy (SEM) (JSM-6010LV, JEOL, Japan) was employed to study the microstructures of the ungrafted and PNIPAm grafted Nylon membranes, both outer surface and cross-sectional area. The cross-sectional surface of the membrane was prepared by cryo-fracture in liquid nitrogen. All surfaces were sputter-coated with gold particles for 60 s before observation. The samples were observed at an accelerating voltage of 15 kV and working distance of 10 mm.

3.3.4 Specific surface area measurement by the Brunauer-Emmett-Teller (BET) method

BET specific surface areas of ungrafted and PNIPAm grafted Nylon membranes were measured by nitrogen adsorption on a Micromeritics ASAP 2010 apparatus. The samples with the weight of 1 g were used and cut into small pieces. Degas pretreatment for BET and pore volume analyses was performed at 110°C for 4 h.

3.3.5 Contact angle measurement

The water contact angle measurment was performed on PNIPAm grafted Nylon membrane in the air at room temperature using the sessile drop method with a goniometer (Dino-Lite Digital Microscope, Taiwan). Droplet of deionized water (3 µL) was placed on the sample’s surface using a syringe. The contact angle was measured immediately after droplet placing. The contact angle reported was an averaged value from five readings ontained by from different places on the same sample.

3.4 Thermo-responsive measurements of grafted membrane

The filtration performance test of Nylon-6 (ungrafted) and PNIPAm grafted membranes were carried out using a filtration apparatus under an operating pressure of 100 kPa. The hydraulic permeability of the ungrafted and PNIPAm grafted membranes at different temperatures, were studied by measuring the water flux. The diameter of the effective membrane area for water permeation was 38 mm. The temperature range of the feedwater in the experiments was from 25 to 45 °C. The operating pressure and temperature were controlled by water flow rate adjustment and hot plate, respectively. The water flux, which is defined as the amount of water permeating through the membrane per unit area per unit time. The water fluxes under the same condition were measured three times and the averaged value was used to plot the curve. Figure 3.3 was shown a schematic diagram of the filtration apparatus. The filtration apparatus consists of 1. Pump, 2. Pressure gauge, 3. Thermometer, 4. Test cell, 5. Permeate water, 6. Flow meter, 7. Pressure valve, 8. Feed tank, 9. Thermostat, and 10. Stirrer. Crossflow filtration was carried out by feedwater was flowed parallel to the membrane surface. In this study, there are two modes of water flow were tested as shown in Figure 3.4. One is cross flow mode as described above. Another one is direct flow, the feedwater supply passes perpendicular through the membrane. In direct flow, these filters require periodic cleaning (or back washing) of membranes. In contrast, a cross flow filtration mode employs a high velocity of raw feedwater flowing in parallel over (across) the membrane surface. This flow keeps the membrane surface from fouling or accumulating solids. The appropriate filtration mode should be selected by taking into account factors such as fluid composition, membrane material, selectivity of the membrane, filtration module geometry, and cleaning methods. Direct flow filtration requires less energy as there is no circulating of feedwater. With cross-flow filtration, the higher velocity of feedwater over the membrane surface (and attendant energy consumption) provides higher filtration rates by reducing membrane fouling (except when filtering very clean feeds). Hence, an economical evaluation and optimization is required for selecting circulating velocity and giving consideration for treatment volume and filtration rate.

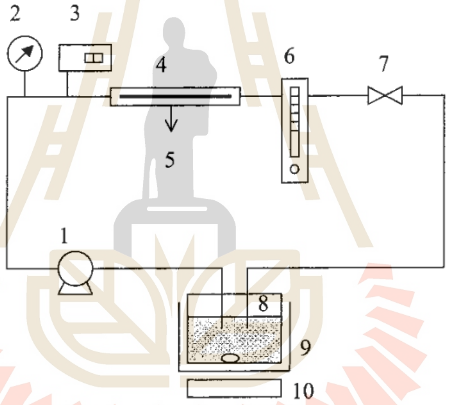
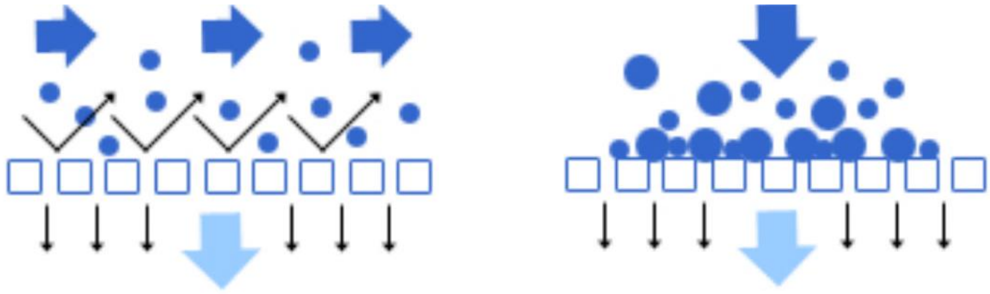


Figure 3.3 Schematic flow diagram of the instrument set-up for filtration experiments (Ito et al., 2002)



(a) (b)

Figure 3.4 Schematic illustration of water flow pass through membrane : (a) cross flow mode, and (b) direct flow mode

3.4.1 Thermo-responsive Gating Performance

The PNIPAm grafted membranes were evaluated for their thermo-responsive open-close switch performance by determining the thermo-responsive gating coefficient (R), which was defined as the ratio of water flux through the membrane at 40°C to that of at 25°C as shown in the equation below (Eq. (3.2)) :

$$R = \frac{J_{40}}{J_{25}} \tag{3.2}$$

where J_{40} and J_{25} are the measured water fluxes at feedwater temperatures of 40 and 25°C, respectively.

3.4.2 Repeatability and Reversibility of Thermo-responsive Gating Switch of Linear and Crosslinked PNIPAm grafted Membranes

The repeatability of the open-close gates performance of the grafted membrane was investigated under the operating pressure of 100 kPa. The measurements were operated at 40°C and 25°C alternately for 10 runs. Before each measurement of water flux at either 40°C or 25°C, the temperature of the feedwater was stabilized at the test temperature for 30 min to ensure that the accomplishment of the thermo-responsive phase transition of the grafted PNIPAm gates.

3.5 Oil-water separation

The oil-water separation ability of PNIPAm grafted membrane was dependent on the grafting yield, the PNIPAm gate structure, and the environmental temperature. The membrane could separate oil-in-water and water-in-oil emulsions at temperatures below and above lower critical solution temperature (LCST) of PNIPAm, at 32°C, respectively.

Chemical :

Paraffin oil, Olive oil, and Tween 20 as a surfactant

Preparation :

First, 5 wt% oil-water emulsion was prepared by mixing the oil and water in a ratio of 5:95 w/w with 1 mg/mL Tween 20 under strong magnetic stirring and shaken for 48 h to obtain a milky solution. Then, 60 wt% oil-water emulsion was prepared by mixing oil and water in a ratio of 60:40 w/w with 1 mg/mL Tween 20 under strong stirring and shaking. Oil-water emulsions with different oils (paraffin and olive oil) were prepared in a similar method.

Procedure :

The as-prepared membrane was placed as filter in Lab filtration apparatus with an inner diameter of 41 mm. At 25°C, the 5 wt% oil-in-water emulsion was poured into the glass funnel, and the separation was achieved by gravity only. At 45°C, the swollen membrane was immersed in the 45°C water to deswell and the excess water on the membrane surface was removed using tissue paper. The 60 wt% oil-water emulsion was heated to 45°C and was poured into the separation setup in an oven set to 45°C to achieve separation. The oil concentration in collected water and the water concentration in the collected oil after separation were determined using an oven by water evaporation and weighing of remaining oil. The separation efficiency was calculated by the following equation (Ou, Wei, Jiang, Simon, & Wang, 2015).

$$\text{S (\%)} = \frac{W_0 - W_1}{W_0} \times 100 \tag{3.3}$$

S is separation efficiency. W_0 (g) is the original oil weigh or water weigh in the feed. W_1 (g) is the oil or water weigh in permeate after filtration.

CHAPTER IV

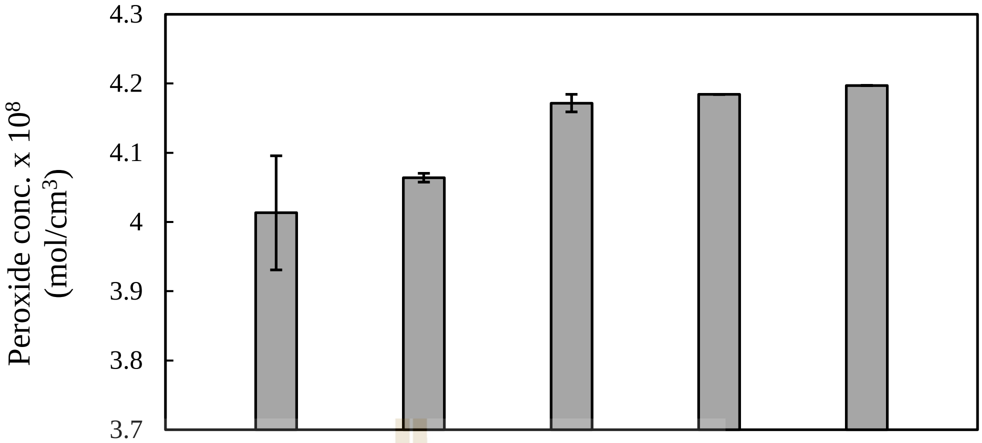
RESULTS AND DISCUSSION

In this chapter, the results were separated into 5 sections. The structure of this chapter is organized as follows. Section 4.1 described the effect of plasma treatment parameters on grafting yield. Section 4.2 presented the effect of time and power of microwave irradiation on grafting yield. The optimum condition was revealed in this section. The effect of grafting yield and PNIPAm gate structures on properties of grafted membranes were described in section 4.3 and 4.4 respectively. Finally, oil-water emulsion separation for their application of the membranes was revealed in section 4.5.

4.1 Plasma treatment

4.1.1 Effect of power input, carrier gas feed rate, and irradiate time on peroxide concentration

The DPPH concentration was quantified using UV-Vis spectroscopy technique. Standard curve showing a linear relationship between the DPPH concentration and absorbance intensity indicated that Beer-Lambert law can be used. The amount of peroxide group on treated membranes could be estimated from a decrease in DPPH concentration as it was used up by the peroxide. While DPPH concentration of the untreated substrate had little to no change, the peroxide concentration of Nylon membranes which were irradiated by argon plasma with different condition were significantly increased, as shown in Figure 4.1.



Power(W)	20	**30***	40	30	30
Argon flow rate (sccm)	5	**5**	5	15	5
Time(min)	1	**1**	1	1	2

Figure 4.1 The peroxide concentration x10^8 (mol/cm^3) of the membrane with different plasma treatment conditions

Figure 4.1 showed peroxide concentration of the treated membranes with different plasma treatment conditions. The plasma treatment with argon flow rate 5 sccm (standard cubic centimeters per minute) under power 30 watts for 1 min was named standard condition*, which has been used in many studies (Ohashi, Chi, Kuroki, & Yamaguchi, 2016). The plasma treatment parameters including power input, carrier gas feed rate, and irradiate time were compared with the standard condition. When the value of each parameter was increased, the peroxide group concentration, as a consequence, also increased. The power input, carrier gas feed rate, and irradiate time were 40 watts, 15 sccm and 2 min respectively, the peroxide group concentration increased to 4.2x10^8 mol/cm^3. While peroxide group concentration of the standard condition was 4.1x10^8 mol/cm^3. The peroxide concentration represented the number of peroxide group on the substrate. Low number of peroxide group on the membrane surface could be infer to that there was also a smaller number of free radicals on the membrane substrate than that of with high number of peroxide group as shown in Figure 4.2. Comparison of the grafting yield of the PNIPAm grafted membrane with 4.1x10^8 mol/cm^3 and 4.2x10^8 mol/cm^3 of peroxide group concentration were shown in Figure 4.3. The treated membrane with Argon flow rate 15 sccm represented the PNIPAm grafted membrane with 4.2x10^8 mol/cm^3 of peroxide group concentration.

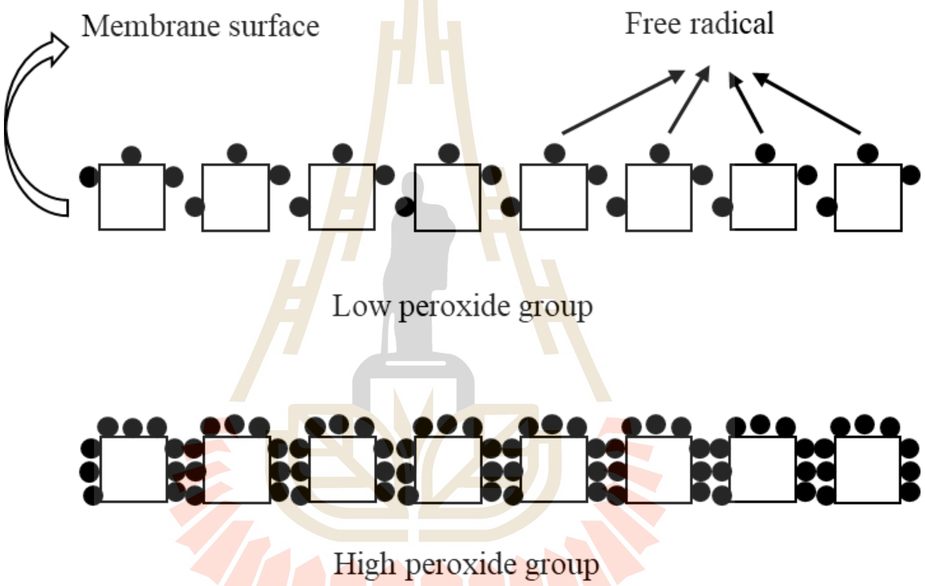
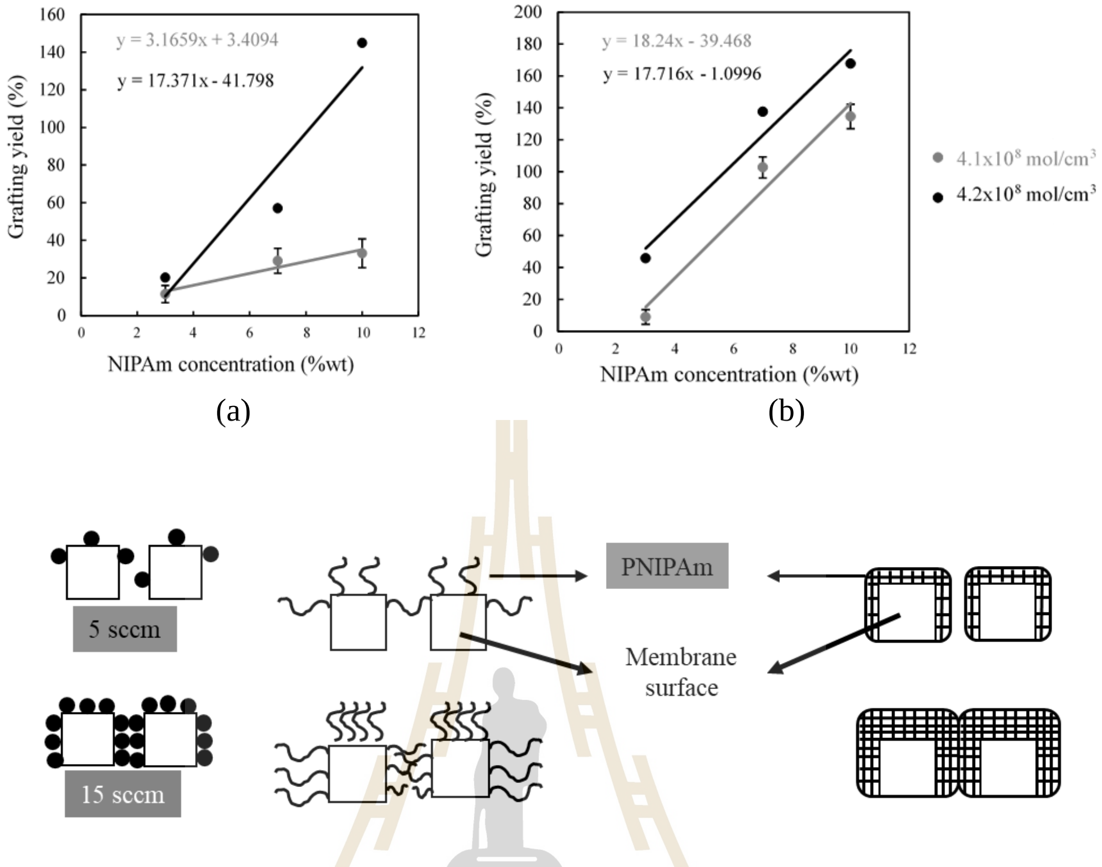


Figure 4.2 Schematic illustration of free radicals on the different membrane surfaces



(a) (b)

(c)

Figure 4.3 Grafting yield of the PNIPAm grafted membrane with 4.1x10^8 mol/cm^3 and 4.2x10^8 mol/cm^3 of peroxide group concentration : (a) linear, (b) crosslinked PNIPAm grafted Nylon membrane, and (c) Illustration of grafted membranes

The treated membranes with 4.1x10^8 mol/cm^3 and 4.2x10^8 mol/cm^3 of peroxide concentrations were grafted with different NIPAm concentrations (3, 7, and 10 wt%) and formed different PNIPAm structures (linear and crosslinked PNIPAm). For both peroxide concentrations of treated membranes, the grafting yield increased with an increasing monomer content. When the peroxide concentration increased from 4.1x10^8 to 4.2x10^8 mol/cm^3, the grafting yield at each monomer content also increased. For linear PNIPAm grafted membrane with $4.1x10^8$ mol/cm^3 of peroxide group, increasing of the grafting yield was relatively low comparing with the grafted membrane with $4.2x10^8$ mol/cm^3 of peroxide group. From Figure 4.3c, not only because smaller number of peroxide group on the top surface and inside the pore surface could be generated, but the linear PNIPAm chains on the top surface and the pore entrance also hindered the diffusion of monomer into the pores, preventing an increase in the length of the polymer chains in the grafting step (Yamaguchi, Nakao, & Kimura, 1996). For crosslinked PNIPAm grafted membrane, the increasing trend of the grafting yield of the membrane with $4.1x10^8$ mol/cm^3 of peroxide group was almost same with that of the membrane with $4.2x10^8$ mol/cm^3. The increasing peroxide group concentration resulted in the increasing of free radicals on the membrane surface. Therefore, chain hindrance in linear PNIPAm was eliminated by grafting the membrane with high peroxide concentration to achieve higher grafting yield.

4.2 Optimization of microwave-assisted graft polymerization

From the concept of using microwave irradiation for heating, the effects of microwave irradiation time and output power on the success of grafting of PNIPAm onto the Nylon porous membrane were investigated.

4.2.1 Temperature measurement of monomer solution in microwave

Because of microwave heating initiated the graft polymerization, the temperature of the solution must be higher than 60°C to assure the decomposition of peroxides to produce alkoxy radicals (Xueqin et al., 2014). The measured temperature of DI water could be assumed as the temperatures of the monomer solution in a microwave. It was due to the temperature of DI water was almost the same as the temperature of the monomer solution with/without crosslinker in a microwave. The temperature measurement of DI water at the different conditions of microwave irradiation was carried out via thermometer. Averaged values of 3 measurements were summarized and tabulated below (Table 4.1).

Table 4.1 The temperature of the monomer solution in a microwave

The temperature of solution (°C)			
Power (W) Time (min)	100	450	800
5	64±0	83±0	85±1
10	68±3	85±1	87±1
15	70±2	90±2	95±3

From Table 4.1, the temperatures of all the conditions were higher than 60°C which was required for peroxide decomposition. When output power or irradiation time increased, the temperature of the solution was also increased. Thus, the graft polymerization could occur in all irradiation conditions. However, the temperature should not be greater than 135°C which was the maximum service temperature of Nylon membrane (Typical data from Whatman Co.).

4.2.2 Grafting yield

The effect of the microwave output power and irradiation time on grafting yield at a constant monomer content of 10 wt% were shown in Figure 4.4. The PNIPAm grafted Nylon membranes with a grafting yield of 0.9-5.9% and 0.3-20.1% were obtained from linear and crosslinked PNIPAm grafted membranes, respectively. Different yields were obtained from using different microwave irradiation time and output power during microwave-assisted polymerization because different temperatures were induced. When the solution temperature was higher than 85°C, the grafting yield was notably increased to higher than 5%. For both the linear and crosslinked PNIPAm grafted Nylon membranes, the condition of microwave irradiation that gave the highest yield was found to be 800 W and 10 min where the solution temperature was as high as 87°C. Note that, with the presence of crosslinker in the monomer solution, grafting yield was about 4 times greater than that of without one.

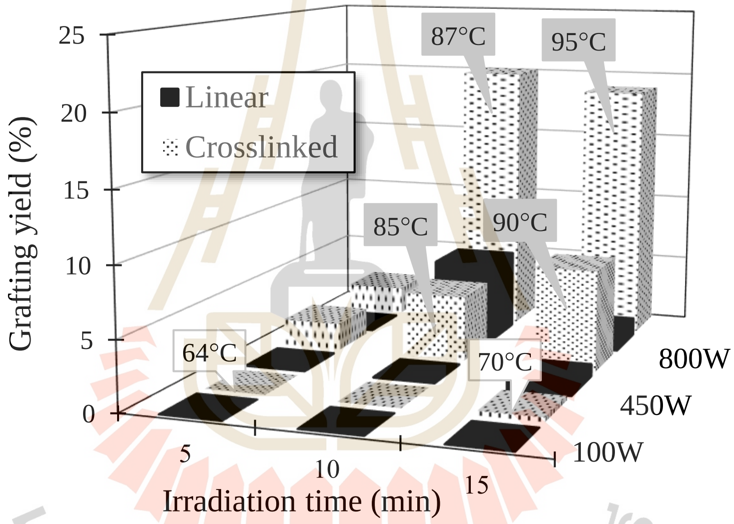


Figure 4.4 Grafting yield of PNIPAm grafted Nylon membrane using different microwave irradiation time and output power with a constant 10 wt% NIPAm solution (Katesripongsa and Trongsatitkul, 2019)

In this novel grafting technique, the temperature of 85°C or above was required to effectively produce alkoxy radicals from the peroxides group (Katesripongsa and Trongsatitkul, 2019). This grafting temperature of 85°C was a lower limit required for significant grafting yield of 5% in both of PNIPAm gate structures. Table 4.1 showed the temperatures of the monomer solution measured using a thermometer immediately after microwave irradiation. The temperatures were varied from 64 to 95°C. However, it should be noted that due to the time lag of the temperature measurement, the actual temperature during the irradiation might be higher than the measured values. In general, the higher output power and longer time gave higher solution temperature resulting in higher free radicals were induced, then higher grafting yields were obtained. These results inferred that the grafting yield was temperature-dependent. However, there seemed to be the limiting or critical temperature that gave the maximum grafting yield. The grafting yield initially increased and then decreased with increasing grafting temperature, while 87°C reached the highest value. This result was similar to that reported by Xueqin et al., (2014). In general, a decrease in grafting yield at elevated temperature was known and accepted as a consequence of accelerating the termination reaction. The temperature increasing caused faster rates of peroxide decomposition, free radical consumption, and termination (Ohashi, Chi, Kuroki, & Yamaguchi, 2016).

4.2.3 Characterization of PNIPAm grafted Nylon membranes

4.2.3.1 FT-IR/ATR analysis

The success of grafting using the novel technique was confirmed by ATR-FTIR technique. FTIR spectra of ungrafted and grafted Nylon membranes were illustrated in Figure 4.5.

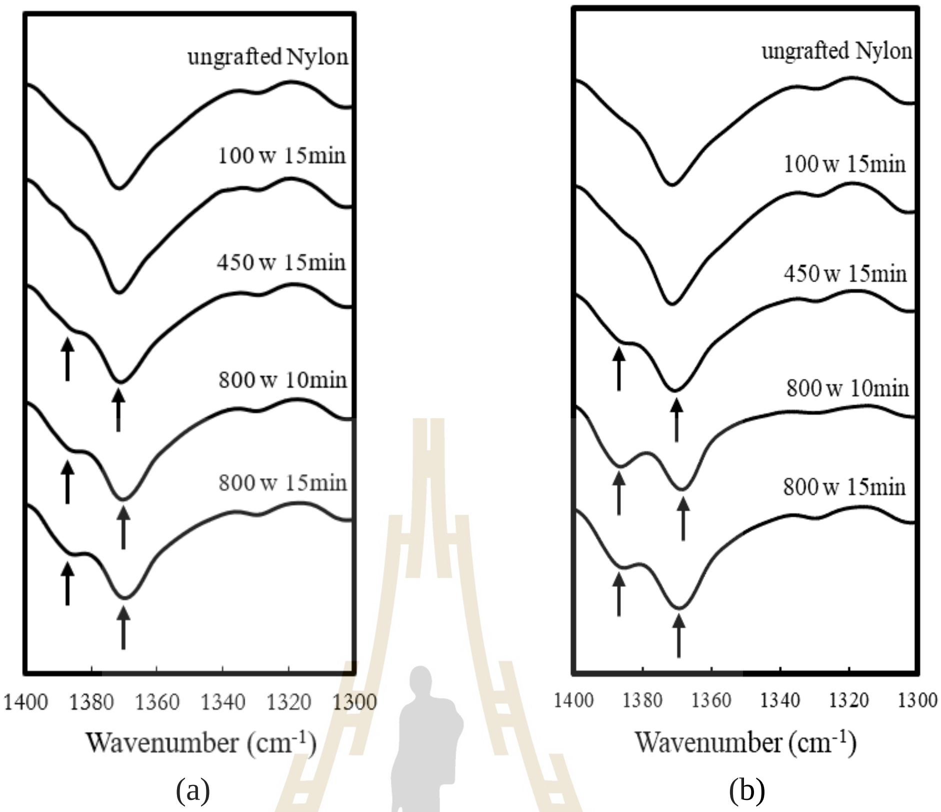


Figure 4.5 FTIR/ATR spectra of membranes : (a) linear, and (b) crosslinked PNIPAm grafted Nylon membrane

Since both the PNIPAm and Nylon-6 membrane possessed an acylamide group (HN-C=O), the characteristic peaks of the acylamide group cannot be used to validate whether PNIPAm was grafted onto the Nylon membranes. However, when compared the spectrum of grafted membrane with that of an ungrafted membrane, new double peaks were found at 1385 cm^{-1} and 1368 cm^{-1}, especially in the spectra of the PNIPAm grafted membranes which the grafting temperature was higher than 85°C. The double peak formed by symmetrical bending vibrations and the coupling split originating from the bimethyl group of the isopropyl group of PNIPAm (Chen et al., 2009). This double peak could be most obviously seen in the spectra of the PNIPAm grafted membranes which was grafted under 800 W for 10 minutes. These results were well agreed with the result of grafting yield as shown above.

4.2.3.2 Morphological analysis

In generally, Nylon membranes were suitable for filtering aqueous solutions and most organic solvents. They were hydrophilic, removing the need for wetting agents when filtering aqueous solutions. The membranes are flexible, durable and tear-resistant (Wang & McCord, 2007). Figure 4.6 showed SEM micrographs of the surface and cross-section of ungrafted Nylon membranes. The Nylon-6 membrane featured with honeycombed porous structures below the skin layer, correspond to the result from Yang, Chu, Li, Zhao, Song, and Chen (2006). SEM micrographs in Figure 4.7 showed the comparing of morphologies of PNIPAm grafted Nylon membrane with/without pressure-assisted permeation for monomer solution. The Figure was a micrograph of cryo-freeze fractured cross-section surface of the grafted membrane. As it was described earlier that, initially the membrane was only immersed in the monomer solution before being irradiated with microwave. Only small amount of monomer molecules in the solution diffused into the pores in the membrane resulting in a dense grafted PNIPAm, mostly onto the top surface of the membrane (Figure 4.7a). Attempting to improve grafting on the entire thickness and uniformity, a pressure-assisted permeation of monomer solution was carried out. Adaptation of coffee maker “Aeropress” was employed to pressurized monomer solution to penetrate into the pores of the membrane. An improvement of grafting was observed as better uniformity of grafted PNIPAm onto the porous Nylon. Higher PNIPAm grafted onto the surface of deeper pores as shown in Figure 4.7b.

The morphologies of the grafted membranes with different grafting conditions were shown in Figure 4.8. For both linear and crosslinked PNIPAm grafted membranes, the grafted PNIPAm apparently filled at the entrance of pores and the top surface of the membrane. With the presence of crosslinker, even denser grafted PNIPAm on the top surface was observed. Under 800 W of microwave irradiation, when irradiation time longer than 15 min (T>95°C), the morphologies of membrane fracture were observed as shown in Figure 4.9. This was suspected to be caused by the actual temperature during the irradiation that was significantly higher than the measured values. In addition, water heated in a microwave oven could be heated above its normal boiling point (superheated). Superheating resulted in boiling points being raised by up to 20°C above their conventional value under microwave irradiation (Whittaker & Mingos, 1994). Superheated water could suddenly produce huge steam. This caused water to boil vigorously and explode. From kinetic aspects of boiling, nucleate bubble formation might made damage to the membrane. The photographs of grafted and fractured Nylon membranes in Figure 4.10 illustrated the rolling and bending of the over heated membrane. They became brittle, some of them cracked and broke into small pieces (Figure 4.10c). This irradiation condition which induced the grafting temperature higher than 90°C, that caused Nylon membrane fracture, was thought to be the upper limit of grafting of the Nylon membrane with PNIPAm polymer. To achieve high grafting yield and prevent fracture of the membrane, the optimum condition of microwave irradiation was concluded to be 800 W and 10 min for both linear and crosslinked PNIPAm grafted onto this Nylon porous membranes. These results were in agreement of the result of grafting yield and chemical composition from FT-IR as shown above.

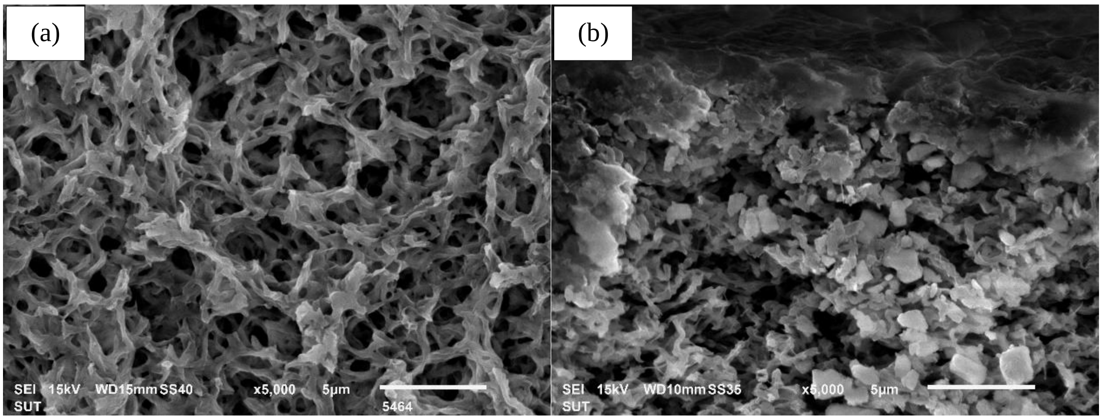


Figure 4.6 SEM micrographs at 5000X magnification of (a) surface and (b) cross-section of Nylon membrane

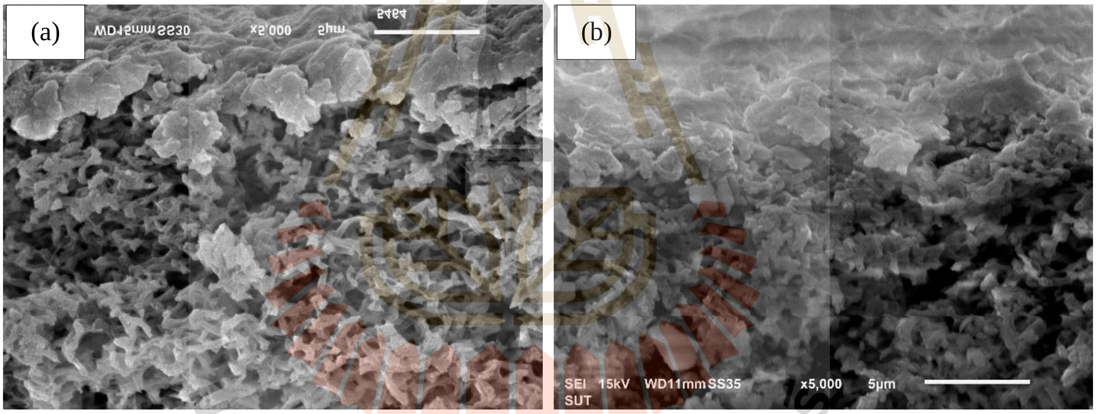


Figure 4.7 SEM micrographs of cross sections of grafted samples at 5000X : (a) without pressure assisted, and (b) with pressure assisted permeation of monomer solution

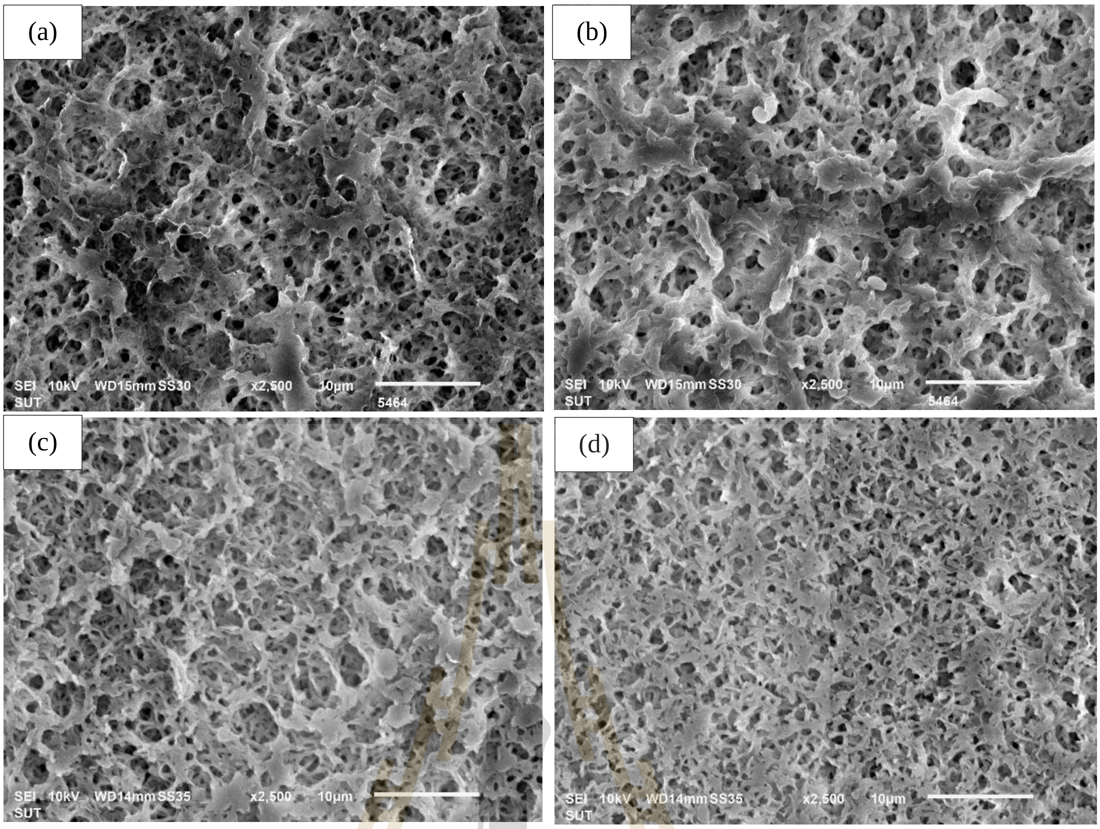


Figure 4.8 SEM micrographs at 2500X magnification of linear and crosslinked grafted membranes respectively : (a), (b) 450W and 15 min (90°C) (c), (d) 800W and 10 min (87°C)

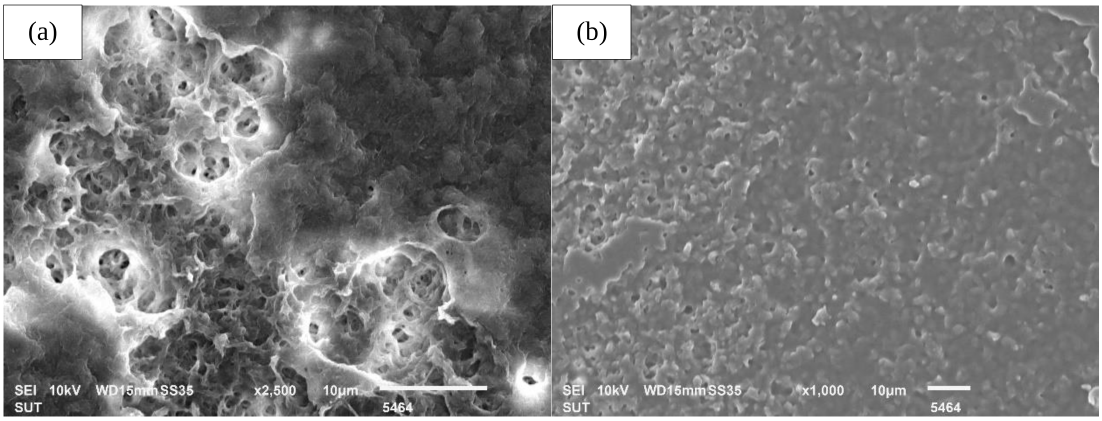


Figure 4.9 SEM micrographs of fractured surface of PNIPAm grafted membranes at 2500X and 1000X : (a) 800W 15 min (linear) and (b) 800W 15 min (crosslinked)

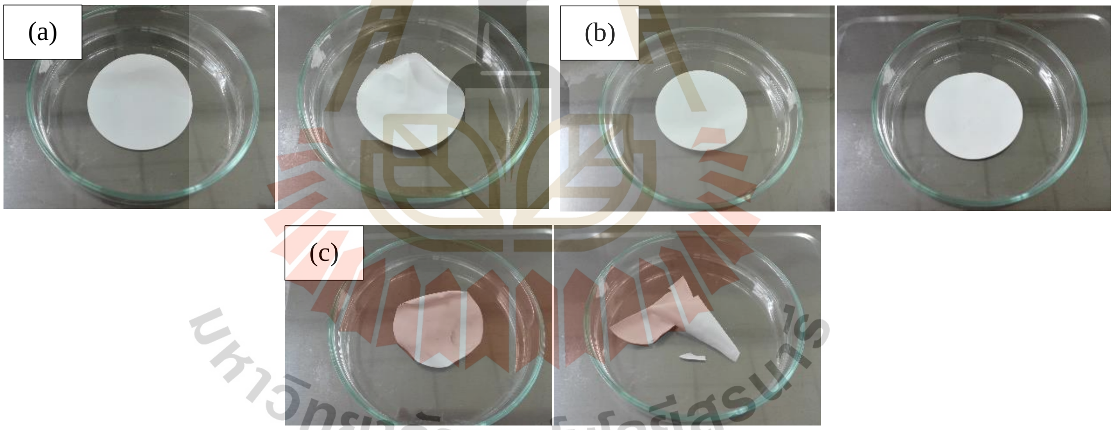


Figure 4.10 Photos of linear and crosslinked grafted membranes respectively by different conditions of microwave irradiation : (a) 450W and 15 min (90°C), (b) 800W and 10 min (87°C), and (c) 800W and 15 min (95°C)

4.3 Effect of grafting yield on properties of grafted membranes

The properties of grafted membrane including chemical composition, morphology, surface properties, and thermo-responsive gating characteristic were studied as a function of grafting yield.

4.3.1 Grafting yield

Graph of grafting yields of PNIPAm grafted membranes which were obtained by using different monomer solution concentrations, were displayed in Figure 4.11. For both PNIPAm structures, the grafting yield increased with increasing monomer concentrations. For linear grafted membrane, the grafting yields increased linearly with the monomer concentration in the range from 2 to 10 wt%. The result showed linear relationship between grafting yield and monomer concentration based on a constant concentration of free radicals. The line was fit with a following linear equation;

$$\text{Grafting yield (\%)} = 4.2 \times \text{NIPAm concentration (\%wt)} \qquad (4.1)$$

At low NIPAm concentration (2-5 wt%), the grafting yields of crosslinked grafted membranes were the same as that of the linear grafted membranes. Thus, the linear equation from eq.4.1 could also be used to estimate the grafting yield of the crosslinked grafted membranes. However, at the high concentration of NIPAm, at 5-10 wt%, grafting yields of crosslinked grafted membranes were quite different from that mentioned above. Their grafting yields at the monomer content from 5-10 wt% were much higher than those at the monomer content from 2-5 wt%. At low NIPAm concentration, there was a low diffusion of NIPAm molecules into the pores, some of monomers in solution were placed and reacted with alkoxy radicals on the top surface only. When the monomer concentration was increased, high diffusion of monomer molecules into the pores was obtained due to higher concentration gradient (Yamaguchi, Nakao, & Kimura, 1991). This result did not occur in linear grafted membrane because of hindering of linear chains on the top surface and the pore entrance in the grafting step (Xueqin, Hidenori, & Takeo, 2014). The grafting yield of crosslinked initially increased with slow rate and then rapidly increased up to 135%. A dramatic transition in the grafting yield occurred as the concentration of NIPAm was higher than 5 wt%.

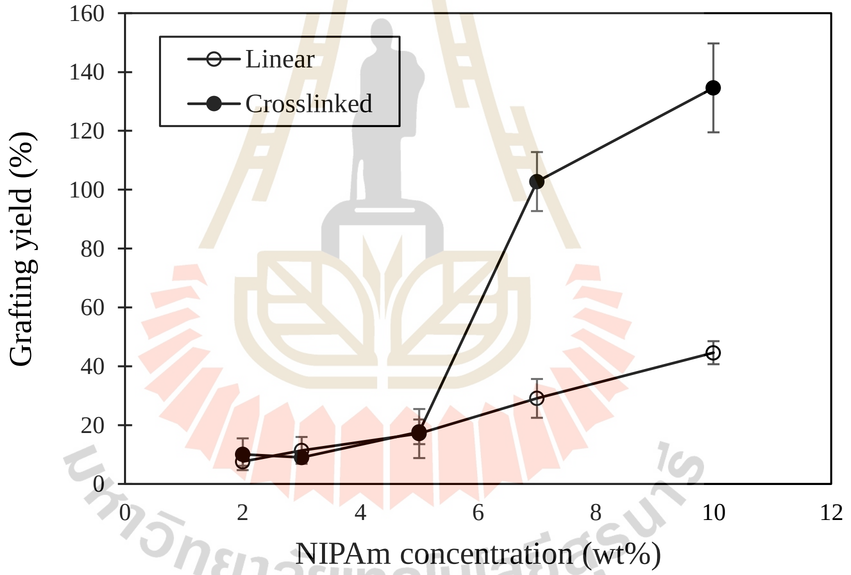
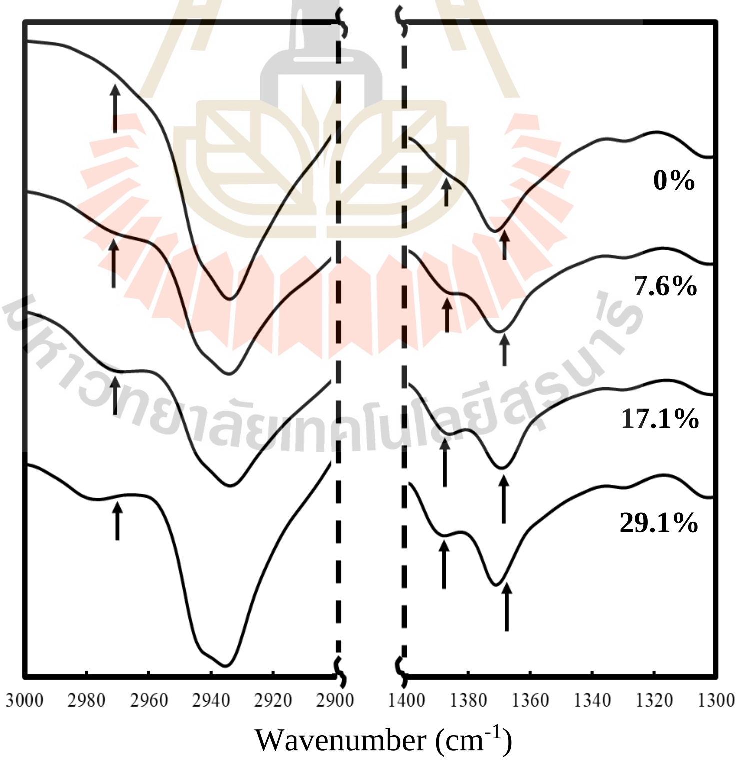


Figure 4.11 Relationship between the grafting yield and NIPAm concentration in the aqueous solutions

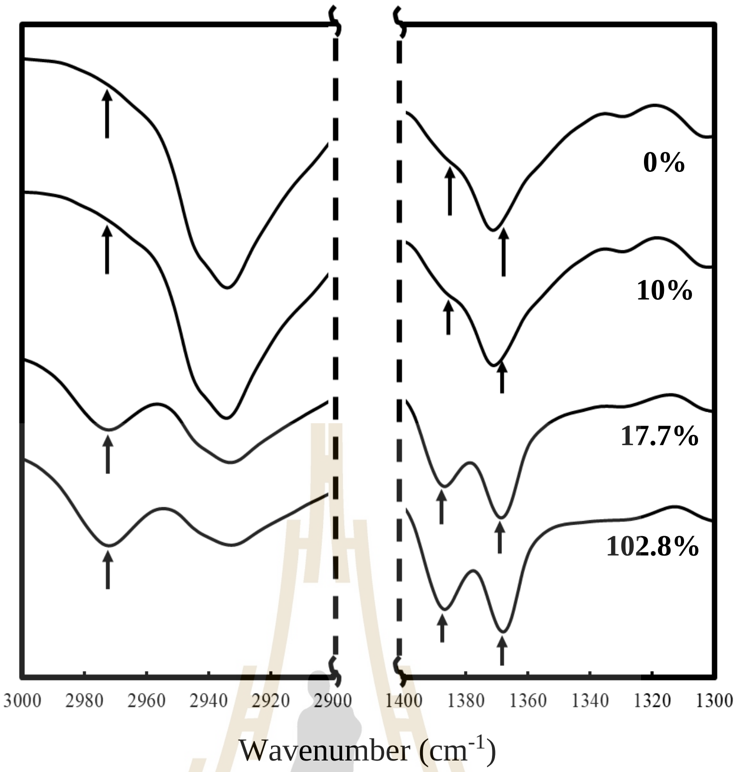
4.3.2 Characterization of PNIPAm grafted Nylon membranes

4.3.2.1 FT-IR/ATR analysis

Confirmation of grafting was revealed from ATR-FTIR spectra in Figure 4.12. The characteristic peaks of PNIPAm at 2970 cm^{-1}, 1385 cm^{-1}, and 1368 cm^{-1} appeared newly in the spectra of the PNIPAm grafted membranes compared with that of the ungrafted membrane. At wavenumber of 2970 cm^{-1} in all of the FT-IR spectra indicated the C-H stretching characterization peak of the methyl group which could be attributed to PNIPAm. The intensity of the characteristic peaks of PNIPAm increased with increasing grafting yield. These results were in agreement with the grafting yield results, which were obtained from weighing technique (Chu et al., 2003).



(a)



(b)

Figure 4.12 FTIR/ATR spectra of : (a) linear and (b) crosslinked PNIPAm grafted Nylon membranes at different grafting yields

4.3.2.2 Morphological analysis

The microstructures of grafted PNIPAm with different grafting yields were investigated by SEM technique. The SEM micrographs of the cross-sectional areas of the grafted membrane were shown in Figure 4.13 and 4.14. For both linear and crosslinked PNIPAm grafted membranes, the grafted PNIPAm located mainly and uniformly on the surface, at the pore entrance of the membrane. With increasing grafting yield, the thickness of PNIPAm grafted membranes became denser. When the grafting yield was high, the grafted PNIPAm formed on the surface and also in the pores of the membrane which could be obviously observed in Figure 4.14b. The PNIPAm skin layer became thicker, resulting in the smaller pore size which was measured using the BET total pore volume. The pore size linearly decreased as the grafting yield increased (as shown in Figure 4.15). From Table 4.2, the BET surface area and total pore volume of linear grafted membrane was decreased with the increasing grafting yield. This corresponded with the pore size of the membrane became smaller. This result was similar to that reported by Choi, Yamaguchi, and Nakao (2000).

Since, the Nylon porous membrane had high volume of pores, a water droplet rapidly spread on the membrane and water permeated through the pore of the membrane. Film of Nylon was used instead of Nylon membrane in the contact angle measurement. The surface property of grafted membrane could be assumed from surface property of grafted Nylon film. The water contact angle of ungrafted Nylon film was approximately 85° at below (25°C) and above LCST (35°C). As shown in Figure 4.16, compared to ungrafted film, the water contact angles of PNIPAm grafted films were lower at 25°C and then increased at 35°C. At below LCST, the contact angle of grafted PNIPAm film was decreased because the stretching PNIPAm chains were wrapped by the water molecules, showing hydrophilicity. While at above LCST, the contact angle of grafted PNIPAm film was increased because the collapsed PNIPAm chains were wrapped by isopropyl groups, showing hydrophobicity. The hydrophilic and hydrophobic behavior switching across LCST was higher with the grafting yield increasing as shown in Figure 4.17. However, when the grafted film significant grafting with 5%, the water contact angle of grafted film was lower than that of ungrafted film at above LCST. This was attributed to the surface tension of the substrate treated by argon plasma was decreased by the formation of hydrophilic groups on the surface (Yamaguchi, Nakao, & Kimura, 1996). Moreover, the influence of hydrophilicity from the curling of the linear PNIPAm chain (Figure 4.18a) and low response of crosslinked PNIPAm network (Figure 4.18b) were suspected. An increasing grafting yield resulted in more surface roughness. Both the surface roughness and the surface free energy increase could yield the more hydrophilicity of surfaces (Feng & Jiang, 2006).

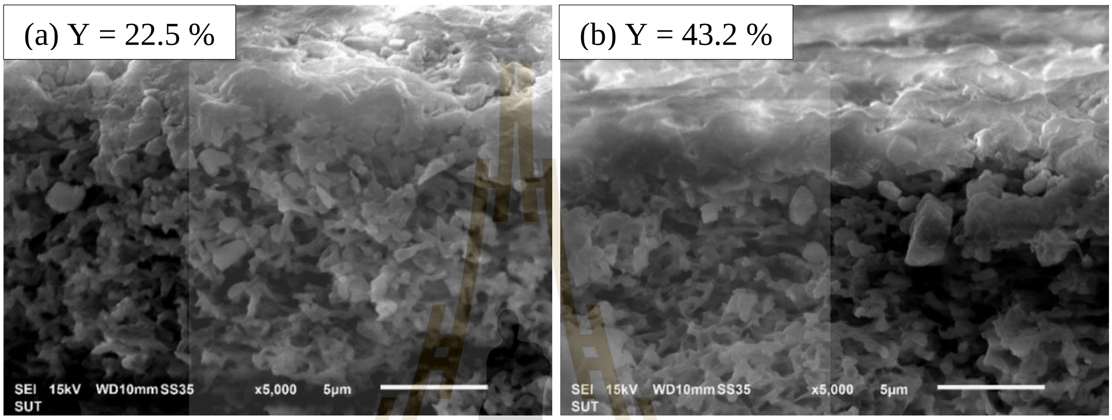


Figure 4.13 SEM micrographs of cross sections of linear grafted membranes

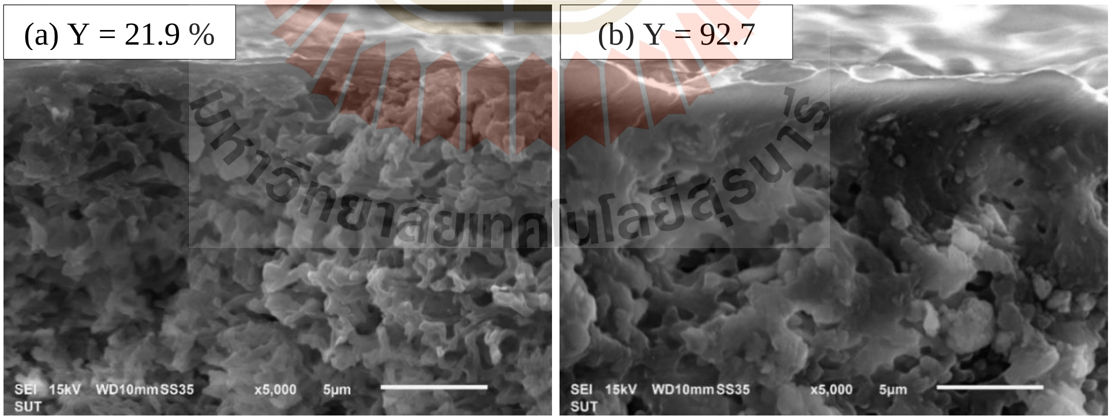


Figure 4.14 SEM micrographs of cross sections of crosslinked grafted membranes

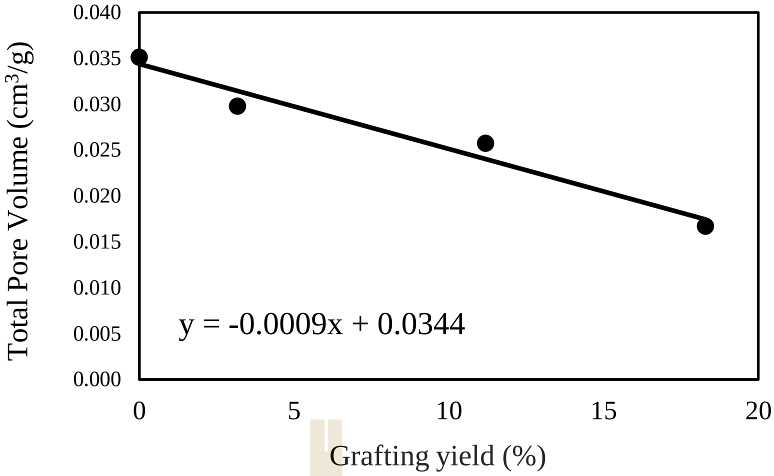
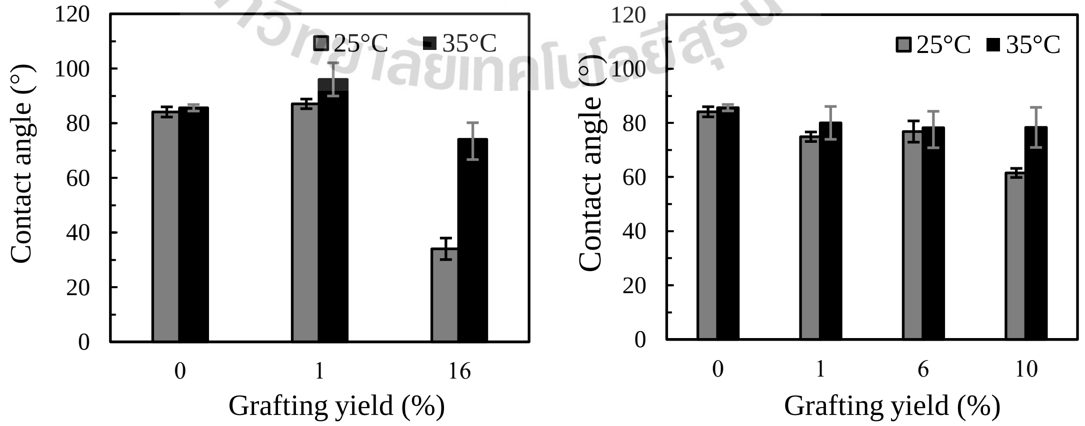


Figure 4.15 Total pore volume of linear PNIPAm grafted membrane with different grafting yields

Table 4.2 Specific surface area of linear grafted membranes

Grafting yield (%)	BET surface area (m^2/g)	Total Pore Volume (cm^3/g)
0	11.25	0.035
3.18	10.29	0.030
11.2	9.61	0.026
18.3	4.69	0.017



(a) (b)

Figure 4.16 Relationship of water contact angles of grafted PNIPAm film and different grafting yields and structures at 25 and 35°C : (a) linear and (b) crosslinked PNIPAm grafted Nylon film

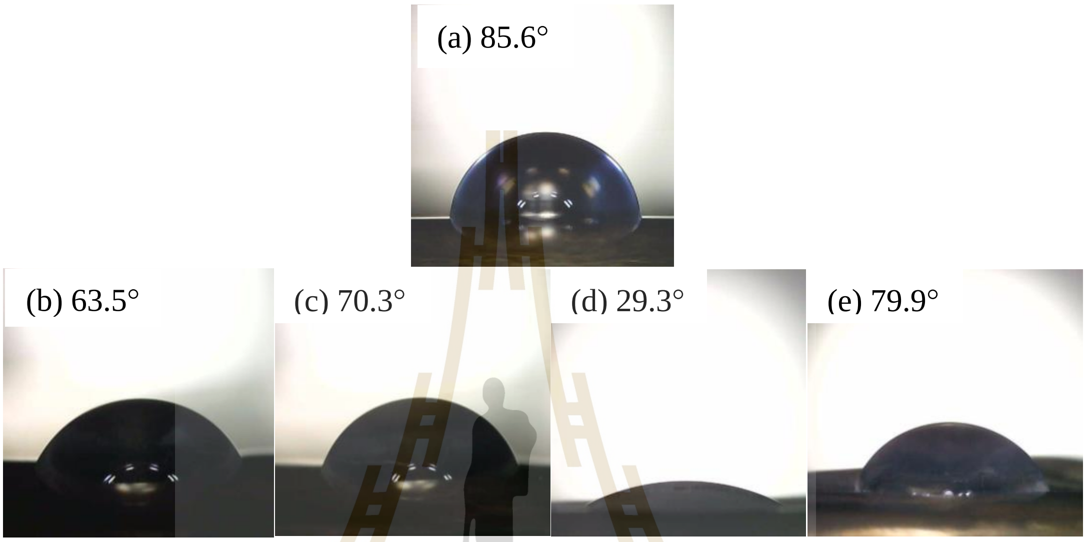
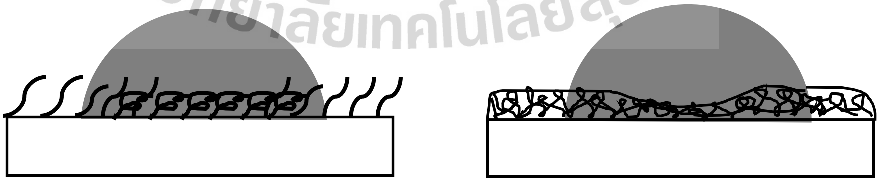


Figure 4.17 (a) Water contact angle of ungrafted film, (b)-(c) Water contact angle of crosslinked PNIPAm grafted membrane (*Y*=10%), (d)-(e) Water contact angle of linear PNIPAm grafted film (*Y*=16%) at 25 and 35°C, respectively



(a) (b)

Figure 4.18 The illustration of water droplet on the film at 35°C : (a) linear and (b) crosslinked PNIPAm grafted film

4.3.2.3 Thermo-responsive Gating Characteristics

The study of thermo-responsive gating characteristics was carried out by water flux through the membrane at temperature across LCST. In this study, the water flux with different water flow mode was observed from 25 to 45°C. The cross flow mode was carried out using filtration experiment in Figure 3.3. Another one was direct flow mode which was measured from glass vacuum microfiltration. The fluxes of water through the ungrafted and PNIPAm grafted Nylon membranes from two flow mode increased simply by increasing the temperature. The phenomenon fits in with Hagen-Poiseuille's law (Eq.4.2) :

$$J = \frac{n\pi d^4 P}{128\eta l} \tag{4.2}$$

where J is the water flux, n is the number of pores per unit area, d is the effective pore size, P is the trans-membrane pressure, η is the viscosity of the flowing liquid, and l is the membrane thickness.

When other parameters were fixed, the flux of water through a membrane at 45°C was always higher than that at 25°C. The above mentioned result was attributed to the reduction in liquid viscosity coefficient with increasing temperature. In addition to the liquid viscosity, the thermo-responsive change of effective pore size by grafted PNIPAm chains was an important factor that significantly affected the water flux at different temperatures. When the feedwater temperature was higher than the LCST, the grafted PNIPAm chains on the inner pore surfaces were in the shrunken and hydrophobic state. As a result, the pore size increased or the pores were opened by the PNIPAm gates and the water flux was high. In contrast, when the feedwater temperature was below the LCST, the grafted PNIPAm chains on the inner pore surfaces were in the swollen and hydrophilic state. Therefore, the pore size decreased or the pores were closed resulting in lower water flux. For the ungrafted membrane, the water flux increased slowly with an increase in the feedwater temperature. This was only due to water viscosity increasing. To eliminate the effect of temperature on water flux, the water measuring fluxes were normalized against the reference temperature (20°C) using equation 4.3 (Yoon, 2015).

$$J_{T_0} = J\left[\frac{42.5+T_0}{42.5+T}\right]^{1.5} \tag{4.3}$$

where J is flux observed, J_{T0} is flux at reference temperature, T is water temperature, and T_0 is reference temperature (20°C).

The water flux through ungrafted membrane should be the same value at all temperature. Thermo-responsive characteristics of water flux through linear and crosslinked PNIPAm grafted membranes, which normalized by the effect of water viscosity were demonstrated in Figure 4.19 and 4.20. For the linear PNIPAm grafted membranes (Figure 4.19), only the membrane with highest grafting yield of 35.7% showed thermo-responsiveness across LCST in cross flow mode. Because of the stronger hydrophobicity, lower frictional drag force was resulted for the water flowing through the membrane. Hence, at low graft yield (4.18%), the water flux of linear PNIPAm grafted membrane at 45°C was larger than that of the ungrafted membrane in cross flow (Figure 4.19a). This result was also found in the study of Chu, Niitsuma, Yamaguchi, and Nakao (2003). In direct flow mode, the grafted membrane with low grafting yield (9-22.5%) showed sharp transition of water flux across LCST. At the temperature of 25-30°C, the water flux slowly increased and then rapidly increased when the temperature increased from 30-35°C. When the temperature of feedwater was higher than 35°C, the water flux was constant at the highest flux of each grafting yield. This behavior demonstrated that linear grafted PNIPAm chains in the membrane pores were able to act as smart thermo-responsive gates both in cross flow and direct flow mode. The thermo-responsive characteristics of the water flux of the membranes with different grafting yields were difference. In direct flow mode, with the increase of grafting yield, the water fluxes mostly decreased at all temperatures. As a result of the pore size decreased with increasing PNIPAm grafted on the inner pore surface and pore entrance. If too much linear PNIPAm was grafted into pores (Y>35.7%), the membrane pores were not be opened anymore even when the grafted PNIPAm chains were in the shrunken state. Accordingly, the water flux through the membrane at temperatures both above and below the LCST tended to zero. Thus, with a too high grafting yield, the grafted PNIPAm chains in the pores were not acted as thermo-responsive gates effectively anymore. For the crosslinked PNIPAm grafted Nylon membranes (Figure 4.20), the water fluxes were almost the same at all temperatures for both of water flow mode. For both of water flow mode, water flux decreased at all temperatures with the increase in grafting yield. Since the increase in the layer of the grafted PNIPAm network at pore entrance with increasing grafting yield, followed by a reduction in pore size. The large decreases were especially observed at the membranes with the grafting yield higher than 8.93% and 92.7% for the cross flow and direct flow mode, respectively. These were called the critical grafting yield that prevented water permeate through the membrane. According to the reduction in pore size, the membrane was choked with too high PNIPAm polymer when the grafting yield higher than the critical grafting yield. However, the crosslinked PNIPAm gates did not show thermo-responsiveness across LCST both in cross flow and direct flow mode. The small thermal response of crosslinked PNIPAm networks resulted in water flux increased slowly while increasing the feedwater temperature from 25–45°C.

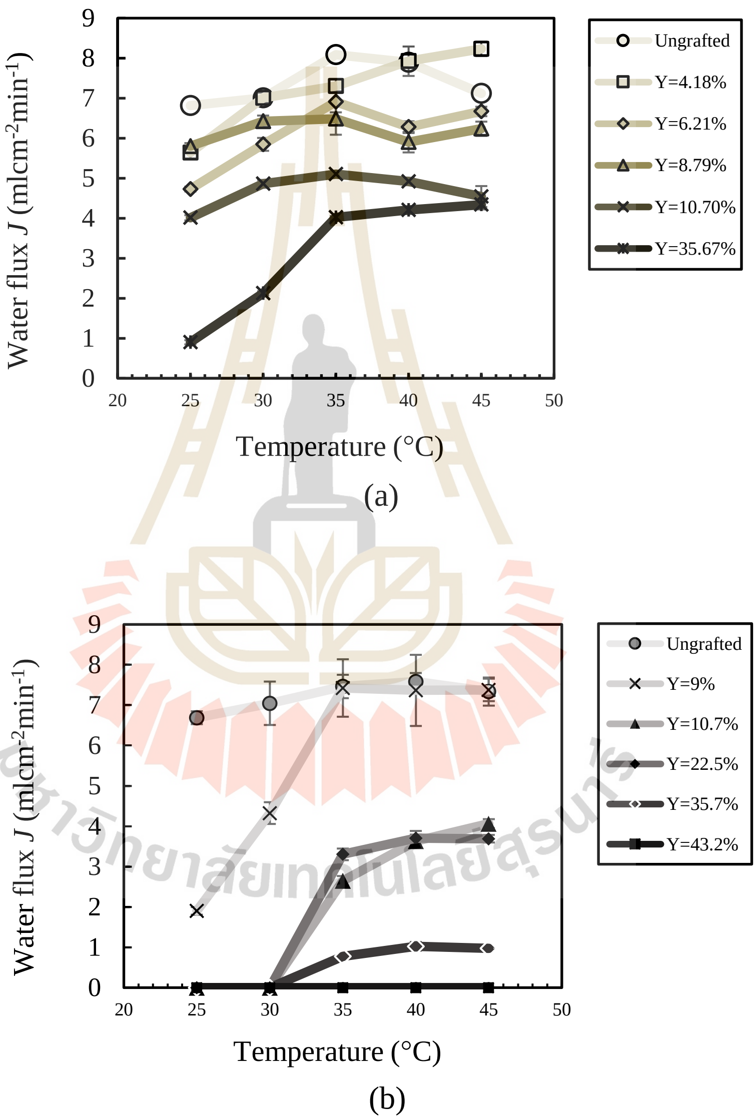


Figure 4.19 Thermo-responsive characteristics of water flux through linear PNIPAm grafted membranes with different grafting yields eliminate effect of water viscosity : (a) cross flow and (b) direct flow mode

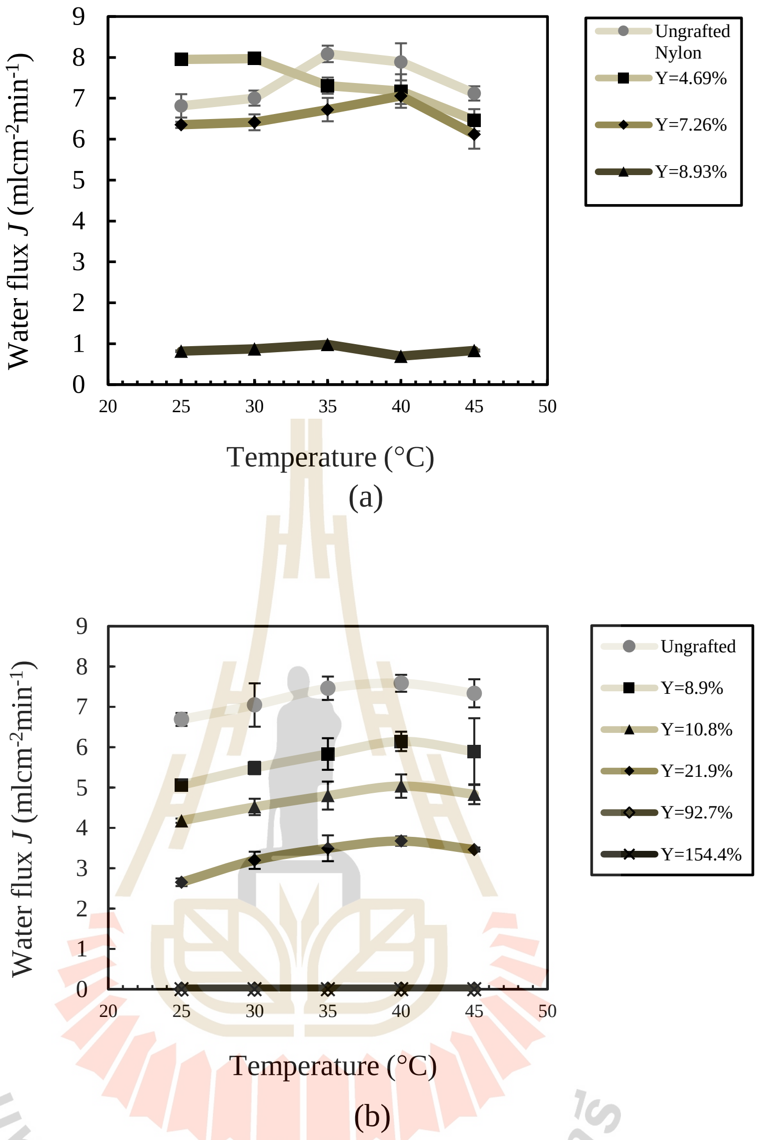


Figure 4.20 Thermo-responsive characteristics of water flux through crosslinked PNIPAm grafted membranes with different grafting yields eliminate effect of water viscosity : (a) cross flow and (b) direct flow mode

4.3.2.4 Thermo-responsive Gating Performance

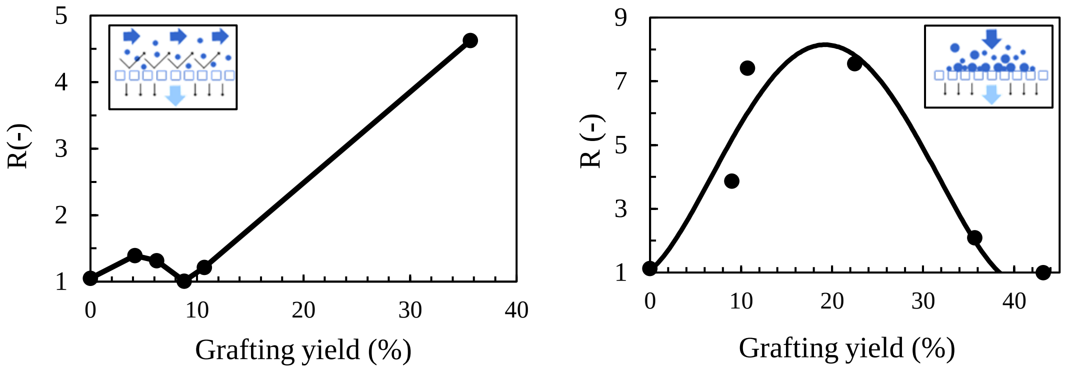
The thermo-responsive open-close switch gating performance of the PNIPAm grafted membranes was evaluated. A specific parameter, which was called the thermo-responsive gating coefficient of the PNIPAm grafted membrane R, was defined as the ratio of water flux through the membrane at 40°C to that at 25°C. From the results of thermo-responsive characteristics of the grafted membrane, these temperatures were used as to represent temperature above and below the LCST of PNIPAm, respectively. Figure 4.21 and 4.22 illustrated the effect of grafting yield on the thermo-responsive gating coefficient of linear and crosslinked PNIPAm grafted membranes with different grafting yields, respectively. The thermo-responsive gating coefficient R was defined as follows (Eq. (4.4)) :

$$R = \frac{J_{40}}{J_{25}} \tag{4.4}$$

where J_{40} and J_{25} are the measured water fluxes at feedwater temperatures of 40 and 25 °C, respectively.

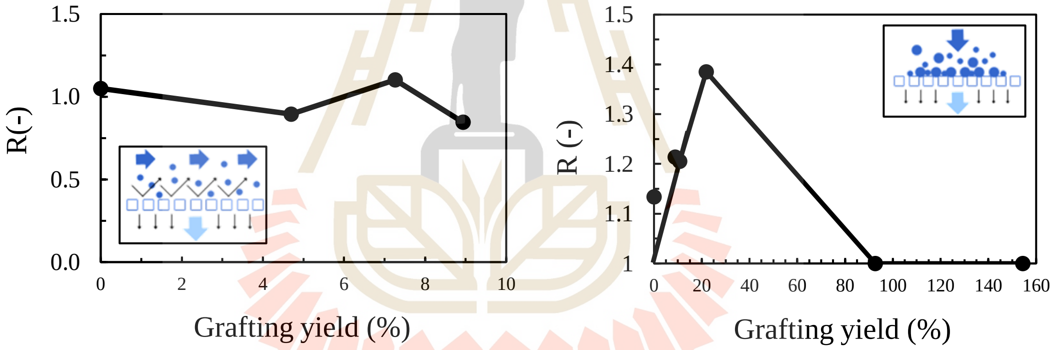
For the ungrafted membrane, the thermo-responsive gating coefficient was always equal to 1.0 because the ungrafted membrane had no thermo-responsive characteristics. For the linear PNIPAm grafted Nylon membranes, only the grafted PNIPAm chains in the membrane pore acted as thermo-responsive gates effectively with the high grafting yield in cross flow mode (Figure 4.21a). Moreover, the critical grafting yield for pore choking was not found. While the thermo-responsive gating coefficient initially increased and then decreased which gave optimum R at 22.5% of grafting yield in direct flow mode (Figure 4.21b). The flux responsiveness coefficient increased with an increase in the grafting yield. However, when the grafting yield was higher than critical grafting yield (35.7%), the pores being choked by the grafted linear PNIPAm. The water flux through the membrane became zero at both 25 and 40°C, and therefore the thermo-responsive gating coefficient was equal to 1. Considering the proper grafting yield of linear PNIPAm grafted Nylon membrane, the thermo-responsive gating coefficient was higher than 3 should be accepted (Chen et al., 2009). In cross flow mode, the linear grafted membrane with the grafting yield of 22% was chosen to be the lower limit. While the linear grafted membrane with the grafting yield of 35% was chosen to be the upper limit in direct flow mode. Therefore, the grafting yield in the range of 22-35% of linear PNIPAm grafted Nylon membrane was suggested for the effective thermo-responsive membrane in both of water flow modes.

In case of the crosslinked PNIPAm grafted Nylon membranes, the thermo-responsive gating coefficient was lower than 1.4 for both of water flow mode. In cross flow mode, the thermo-responsive gating coefficient of the grafted membranes with the grafting yield of 0-9% were almost the same at approximately 1 (Figure 4.22a). However, the optimum R of 1.4 was obtained from the crosslinked PNIPAm grafted membrane with 21.9% of grafting yield in direct flow mode. The thermo-responsive gating coefficient initially increased and then decreased with an increase in the grafting yield as same as the linear PNIPAm grafted membrane. The critical grafting yield of crosslinked PNIPAm gate for choking the membrane pores was as high as 92.7% (Figure 4.22b). Thus, the grafting yield in the range 21-92% of crosslinked PNIPAm grafted Nylon membrane was suggested for the effective thermo-responsive gating membrane in both of water flow mode.



(a) (b)

Figure 4.21 Thermo-responsive gating coefficient, R of linear grafted membranes : (a) cross flow and (b) direct flow mode



(a) (b)

Figure 4.22 Thermo-responsive gating coefficient, R of crosslinked grafted membranes : (a) cross flow and (b) direct flow mode

4.4 Effect of PNIPAm gate structures on properties of grafted membranes

The properties of grafted membrane including morphology, surface properties, thermo-responsive gating characteristics and repeatability of thermo-responsive gating switch were studied from the results of different PNIPAm gate structures.

4.4.1 Characterization of PNIPAm grafted Nylon membranes

The characteristics of both linear and crosslinked PNIPAm grafted membranes were compared with almost the same grafting yield. From FT-IR spectra in Figure 4.12, the addition of the crosslinker showed the intensity of the PNIPAm characteristic peak almost the same as compared to that of without one at the same grafting yield.

4.4.1.1 Morphological analysis

At almost the same grafting yield, the microstructures of both PNIPAm structure grafted on the membrane were different. From Figure 4.23a, the linear PNIPAm structure which discontinuity with an irregular form attached to the top surface and pore entrance of the Nylon membrane, while the crosslinked structure looks like a flat thin sheet continuously placed on the top surface of the Nylon membrane, as shown in Figure 4.23b. The plausible explanation was that the addition of the crosslinkers formed crosslinked network with some of the monomer in the solution. Instead of all crosslinked PNIPAm network was grafted on the activated surface, they connected the chains together as a network only on the top surface. The thickness of the grafted layer in the crosslinked PNIPAm structure was thinner than that in the linear PNIPAm grafted membrane (Chen et al., 2009). The crosslinked PNIPAm structure had a compact with the continuous network as the thin film that coated on the surface. The different microstructures of both membranes had an influence on their properties especially the thermo-responsive gating performance.

The water contact angle of both linear and crosslinked grafted membranes with very high grafting yield (>100%) could be measured using the sessile drop method. They could be used in the test because the pores mostly being choked by the grafted PNIPAm. They were compared with ungrafted Nylon film (assume as membrane) and were shown in Figure 4.24 and 4.25. When the temperature increasing from 25 to 35°C, the linear grafted membrane exhibited changes in water contact angle higher than the crosslinked grafted membrane. When the crosslinked PNIPAm grafted membrane had a very small change in response to the temperature as compared with the ungrafted Nylon membrane. Its change in water contact angle was almost the same as the ungrafted Nylon membrane. The switch of the surface property between hydrophilicity and hydrophobicity which responded to the temperature represented their thermo-responsive behavior. This revealed that the linear PNIPAm grafted membrane had a better thermo-responsive behavior of surface switching than crosslinked PNIPAm grafted membrane. A plausible explanation was the crosslinked PNIPAm grafted membrane used a long time to respond in the temperature of a water droplet. Corresponding with the response time for pore opening or closing was very short (within 30 s). In contrast, the response time of cross-linked thermosensitive gels was more than 10 min or hours which were obtained from Yamaguchi, Ito, Sato, Shinbo, and Nakao (1999).

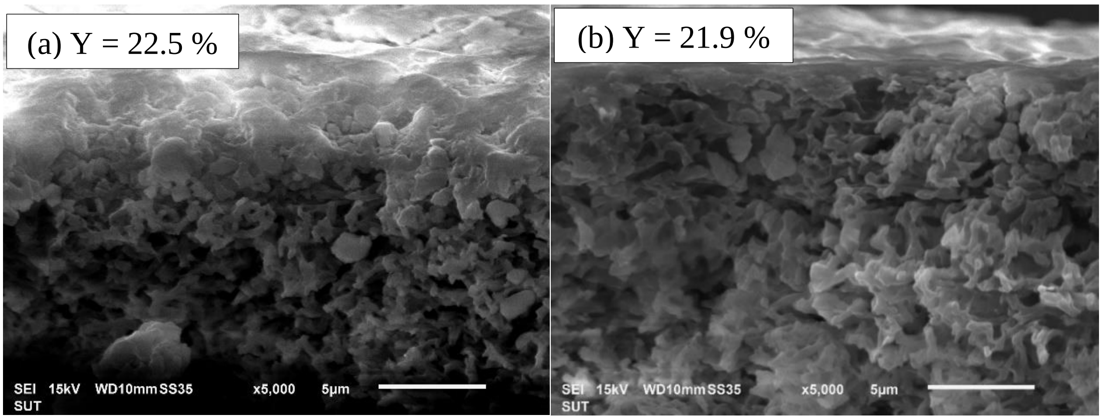


Figure 4.23 SEM micrographs of cross sections of (a) linear, and (b) crosslinked PNIPAm grafted Nylon membrane

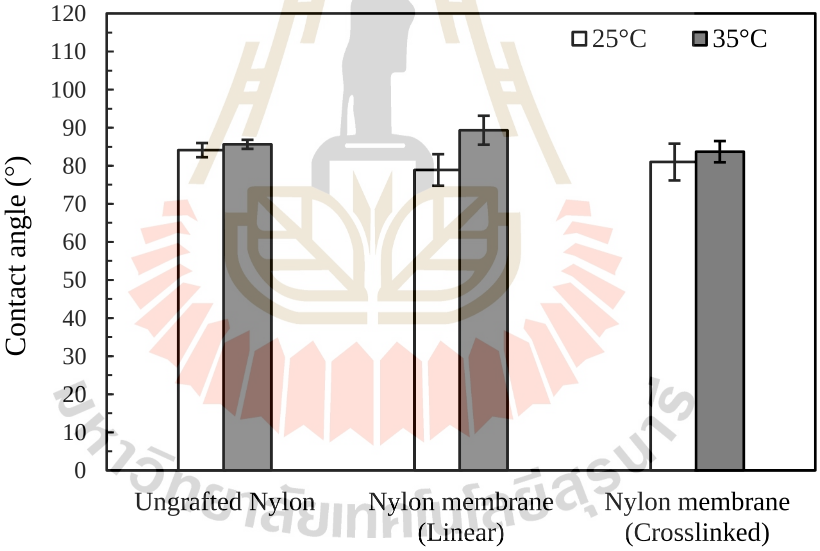
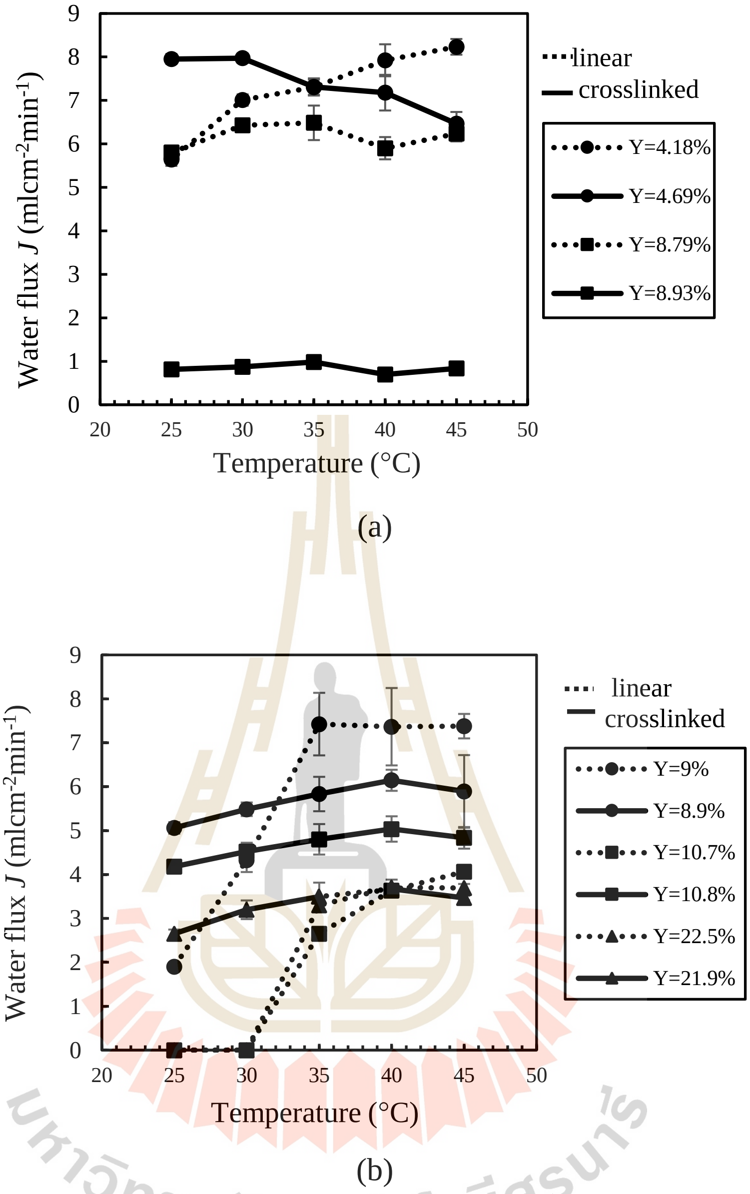


Figure 4.24 Relationship between water contact angles of grafted PNIPAm membranes structures at 25 and 35°C

Figure 4.25 Water contact angle of : (a) ungrafted, (b) linear, and (c) crosslinked PNIPAm grafted membrane at 35°C

4.4.1.2 Thermo-responsive Gating Characteristics

Comparing the water flux at different temperatures of the linear grafted membrane with those of the crosslinked grafted membrane was shown in Figure 4.26. In cross flow mode, only the linear PNIPAm grafted membranes with 4.18% showed thermo-responsiveness across LCST and performed as thermo-responsive membrane. The water flux of this membrane increased from 6 to 8 ml $cm^{-2}min^{-1}$ with the temperature increasing from 25 to 45°C. Because the crosslinked network structures of grafted PNIPAm layers had more compact than the linear PNIPAm chains with free ends, very small and slow response to the temperature than linear PNIPAm grafted membranes. However, its water flux did not show sharp response occurred around 32°C (Figure 4.26a). In contrast, the dramatic transition across 32°C was observed on the water flux of linear PNIPAm grafted membrane in direct flow mode. While the crosslinked PNIPAm grafted membrane showed small response to the temperature increasing from 25-45°C (Figure 4.26b). Therefore, the membrane grafted with linear PNIPAm structure exhibited the thermo-responsive membrane with sharp transition in water flux across LCST higher than crosslinked PNIPAm grafted membrane.



(a)

(b)

Figure 4.26 Thermo-responsive characteristics of water flux through linear and crosslinked PNIPAm grafted membranes with the same grafting yields eliminate effect of water viscosity : (a) cross flow and (b) direct flow mode

With the same grafting yield, the microstructure of grafted PNIPAm near the grafted surface on the linear grafted membrane was denser than that of crosslinked grafted membrane. The pore size of membranes was estimated using Hagen-Poiseuille equation (4.5).

$$J = \frac{\varepsilon \cdot r^2}{8 \cdot \mu \cdot \tau} \cdot \frac{\Delta P}{d} \tag{4.5}$$

where J is the water flux that measure from the experiment, ε is porosity of Nylon-6 membrane (≈0.4) (Chakrabarty, Saha, and Ghoshal, 2010), τ is tortuosity (≈2), μ is the viscosity of feedwater, ΔP is hydraulic pressure difference, r is pore radius, and d is the membrane thickness.

The estimated pore size of the membranes at different feedwater temperatures in both of flow mode were shown in Table 4.3 and 4.4. When the gate opened completely at 45°C, the pore size of linear PNIPAm grafted membranes were higher than those of the crosslinked grafted membrane. This was attributed to a flat thin sheet of crosslinked PNIPAm on the membrane surface that blocked the pore entrances even at above LCST. The crosslinked PNIPAm gate did not respond to the change in temperature and feedweter could not penetrated through the membrane. In cross flow mode, the pore size of crosslinked grafted membrane did not change or decrease when the gate closed completely at 25°C. While pore size of liner membrane small decreased from 0.23 to 0.19 μm at 4.18% of grafting yield. However, at higher grafting yield (≈9%) showed obvious difference of both structures. The pore size of crosslinked PNIPAm grafted membrane highly decreased to 0.07 μm. While the pore size of linear

PNIPAm grafted membrane normally decreased to 0.20 µm. This might be due to a much crosslinked PNIPAm network on the membrane surface that fully blocked the pore entrances. In direct flow mode, the pore size of liner membrane highly decreased from 0.22 to 0.11 µm at 9% of grafting yield. Moreover, at higher grafting yield (10.7 and 22.5%) showed the pore size decrease from 0.16 to the gate closed completely as 0 µm. While the pore size of crosslinked PNIPAm grafted membrane small decreased of 1-2 µm with the temperature decreasing from 45 to 25°C. Comparison of two different PNIPAm gate structures, the linear PNIPAm gate performed as thermo-responsive gate effectively, while the crosslinked PNIPAm network did not perform as the thermo-responsive gate.

Table 4.3 Pore size of the membranes at different temperatures in cross flow mode

Structure	Grafting yield (%)	Pore size (µm) at temperature (°C)				
		45	40	35	30	25
Ungrafted Nylon	0	0.22	0.23	0.23	0.22	0.21
Linear	4.18	0.23	0.23	0.22	0.22	0.19
	8.79	0.20	0.20	0.21	0.21	0.20
Crosslinked	4.69	0.21	0.22	0.22	0.23	0.23
	8.93	0.07	0.07	0.08	0.08	0.07

Table 4.4 Pore size of the membranes at different temperatures in direct flow mode

Structure	Grafting yield (%)	Pore size (µm) at temperature (°C)				
		45	40	35	30	25
Ungrafted Nylon	0	17.08	17.33	17.29	16.76	16.10
Linear	9	0.22	0.22	0.22	0.17	0.11
	10.7	0.16	0.15	0.13	0	0
	22.5	0.16	0.16	0.15	0	0
Crosslinked	8.9	0.20	0.16	0.16	0.17	0.18
	10.8	0.18	0.18	0.18	0.17	0.17
	21.9	0.15	0.16	0.15	0.15	0.13

4.4.1.3 Thermo-responsive Gating Performance

The thermo-responsive gating coefficient of linear PNIPAm structure was compared with those of the crosslinked structure. The comparison of thermo-responsive gating coefficient R from both of water flow modes were shown in Table 4.5 and 4.6. The highest thermo-responsive gating coefficient R of linear grafted membrane with 4.18% grafting yield was only 1.4 in cross flow mode. This was the best gating property in this comparison (Table 4.5). In direct flow mode, thermo-responsive gating coefficient of linear PNIPAm structure was higher than crosslinked PNIPAm structure and ungrafted membrane, respectively. The highest thermo-responsive gating coefficient was 7.5 at the linear PNIPAm grafted membrane with 22.5% of grafting yield (Table 4.6). From both of two flow modes, the comparison showed that thermo-responsive open-close switch performance of the linear PNIPAm grafted membrane was much better than that for the crosslinked PNIPAm grafted membrane.

Table 4.5 Thermo-responsive gating coefficient, R of different PNIPAm gate structure in cross flow mode

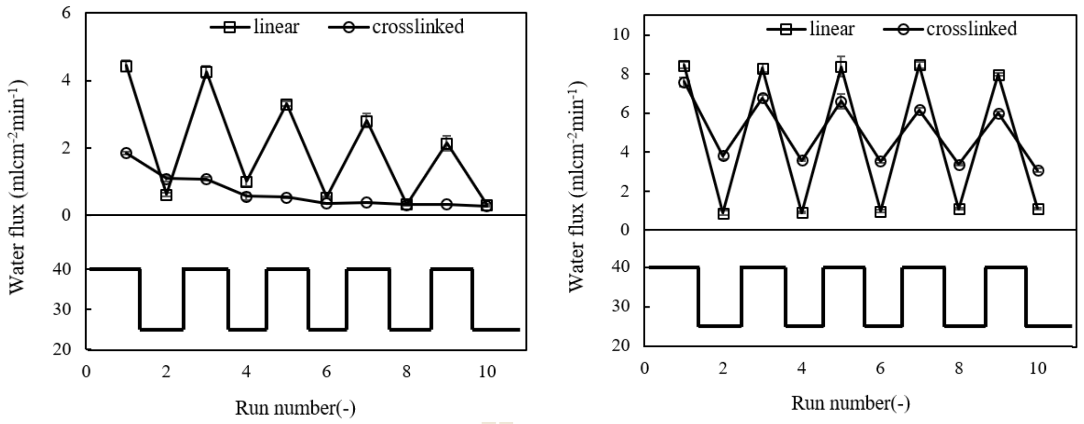
Structure	Grafting yield (%)	Water flux at temp (°C)		R
		25	40	
Ungrafted Nylon	0	7.11	7.46	1.0
Linear	4.18	5.63	7.85	1.4
	8.79	5.80	5.84	1.0
Crosslinked	4.69	7.95	7.11	0.9
	8.93	0.81	0.69	0.8

Table 4.6 Thermo-responsive gating coefficient, R of different PNIPAm gate structure in direct flow mode

Structure	Grafting yield (%)	Water flux at temp (°C)		R
		25	40	
Ungrafted Nylon	0	7.5	6.7	1.1
Linear	9	7.3	1.9	3.8
	10.7	3.6	0.0	7.3
	22.5	3.7	0.0	7.5
Crosslinked	8.9	6.1	5.1	1.2
	10.8	5.0	4.2	1.2
	21.9	3.6	2.6	1.4

4.4.1.4 Reversibility and repeatability of thermo-responsive open-close gating switch of linear and crosslinked PNIPAm grafted membranes

The stability of the grafted PNIPAm gates in the membrane pores for long-term operations was examined. The reversibility and repeatability of thermo-responsive open-close gating switch of grafted membranes was investigated. Their results were shown in Figure 4.27. Both linear and crosslinked PNIPAm grafted membranes with the highest thermo-responsive gating coefficient were chosen for the reversibility and repeatability experiments. In cross flow mode (Figure 4.27a), linear and crosslinked PNIPAm grafted membranes exhibited unstable gating characteristics within 10 runs of operation. At the temperature higher LCST (40°C), the water flux through the linear grafted membrane dropped in every single cycle. The water flux dramatically decreased in one cycle, extremely tend to zero for the crosslinked grafted membrane. This revealed that linear PNIPAm gates grafted in membranes had the repeatability of thermo-responsive open-close switch performance within 10 runs, but could not reverse to the original water flux. The crosslinked PNIPAm gates grafted in membranes could not reversibility and repeatability of thermo-responsive open-close gating switch performance. For direct flow mode (Figure 4.27b), both linear and crosslinked PNIPAm grafted membranes exhibited stable gating characteristics within 10 runs of operation. The water fluxes of both membranes at 40°C and 25°C had little to no change when the feedwater temperature returned to 40°C from 25°C or returned to 25°C from 40°C in the cycles. Because difference of water flow modes resulted in the different thermo-responsive open-close gating switch performance. With the same operating pressure of 100 kPa, it was easier for water in direct flow to pass through the membrane than water in cross flow, resulting in a shorter time for water filtration experiment. The time was measured when a given amount of water passes through the membrane. This might plausibly be that a long time operating to the experiment with high water pressure made the PNIPAm gates relaxing, which facilitated polymer chains disengagement leading to the plastic deformation in the polymer (Balogun & Mo, 2014). Hence, the linear and crosslinked PNIPAm gates grafted in membranes showed both reversibility and repeatability of thermo-responsive open-close gating switch performance in experiment of direct flow mode but only repeatability for linear PNIPAm grafted membrane in cross flow mode.



(a) (b)

Figure 4.27 Repeatability of “open-close” switch of linear and crosslinked grafted PNIPAm gates in the membrane pores : (a) cross flow and (b) direct flow mode

4.5 Oil-water separation

This smart membrane with switchable hydrophilicity and hydrophobicity considered feasible for oil−water separation. The membrane was hydrophilicity at the temperature below the LCST and became hydrophobicity at a temperature above the LCST of PNIPAm. A hydrophilic membrane was suitable for separating oil-in-water emulsions, while a hydrophobic membrane separated water-in-oil emulsions.

The contact angle of paraffin oil and olive oil compaing with a water droplet on the Nylon film were shown in Table 4.7. The contact angle of oils and water on the Nylon surface were used to represent interfacial tension and compatibility between oils and water. The oil and water should combine to achieve the emulsion easily if their contact angles are almost the same. Interfacial tension or surface tension is a property of liquids that is governed by intermolecular interactions (Domańska & Królikowska, 2010). It originates from the cohesive forces between molecules in a liquid. The contact angle as a function of liquid surface energy measured on various surfaces. Liquids shape in such a way that the minimum surface area per volume of a spherical droplet. In this study the contact angle of paraffin oil was higher than that of the olive oil about 10°. Comparing their contact angles with water, paraffin oil showed the contact angle near to water than olive oil. So, water should be compatible with paraffin oil more than olive oil. As a result, the stability of the paraffin oil-water emulsion was more stable than olive oil-water emulsion when used the same preparation. The olive oil-water emulsion was instable and easy to separate, resulting in better separation efficiency. In addition, the polarity of paraffin oil was higher than olive oil which resulted from the O-H group in the chemical structure was a plausible explanation of their oil-water emulsion stability.

Table 4.7 The water contact angle of different oil on Nylon film at room temperature

Water	**Paraffin oil**	**Olive oil**
84.11±2°	**28.55±4°**	**19.14±3°**
		

4.5.1 Influence of grafting yields on separation efficiency

For oil-in-water emulsion separation, the grafted membrane was used in the separation apparatus at low temperature (T<LCST). The hydrophilic membrane could separate olive oil-in-water emulsion with higher separation efficiency than

paraffin oil-in-water emulsion (Figure 4.28). This was due to the paraffin oil-water emulsion was much more stable than the olive oil-water emulsion as discussed above. The paraffin oil was relatively better dispersed in water more than olive oil. At low temperature, the PNIPAm grafted membrane as the hydrophilic surface traped water, as a consequence the water-trapped surface repels oil due to the repellency between polar and non-polar molecules (Zhang, Zhang, & Wang, 2012). The PNIPAm grafted membrane with higher grafting yield exhibit better separation ability as shown in Figure 4.28. With decreasing of pores size, it became harder for oil droplets to pass through the pores. Only water selectively permeated through the hydrophilic membrane. Therefore, excellent separation efficiency was achieved. The highest separation efficiency of 99.7% was obtained from the linear PNIPAm grafted membrane with 35.67% of grafting yield. In the case of water-in-oil emulsions (Figure 4.29), the grafted membrane with separation apparatus was placed in an oven at high temperature 45°C (T>LCST). The hydrophobic membrane could only separate water-in-paraffin oil with poor separation efficiency (<1%). Although, the membrane showed hydrophobicity at a temperature above LCST. Unlike oil-in-water emulsions, the separation of water-in oil emulsions occurs through a combination of two processes. First, water-in-oil emulsions demulsify into water phase and oil phase via electrostatic coalescence (Kwon et al., 2012). Oil with a density lower than that of water could float on the surface of the water. Hence, oil was blocked when the hydrophobic surface of the membrane was covered by water. Moreover, it was even harder for oil to pass through the pores those were blocked by water with increasing grafting yield. The optimum efficiency was observed at linear PNIPAm grafted membrane with 10.7% of grafting yield.

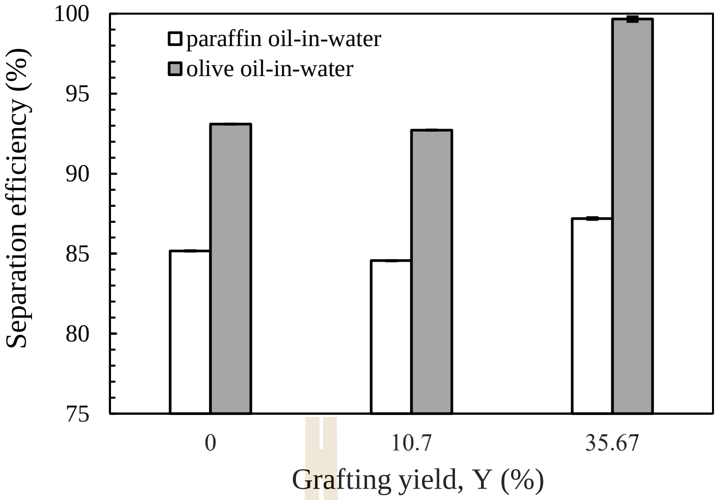


Figure 4.28 Separation efficiencies of linear PNIPAm grafted membrane with different grafting yield for separating oil-in-water emulsions at low temperature

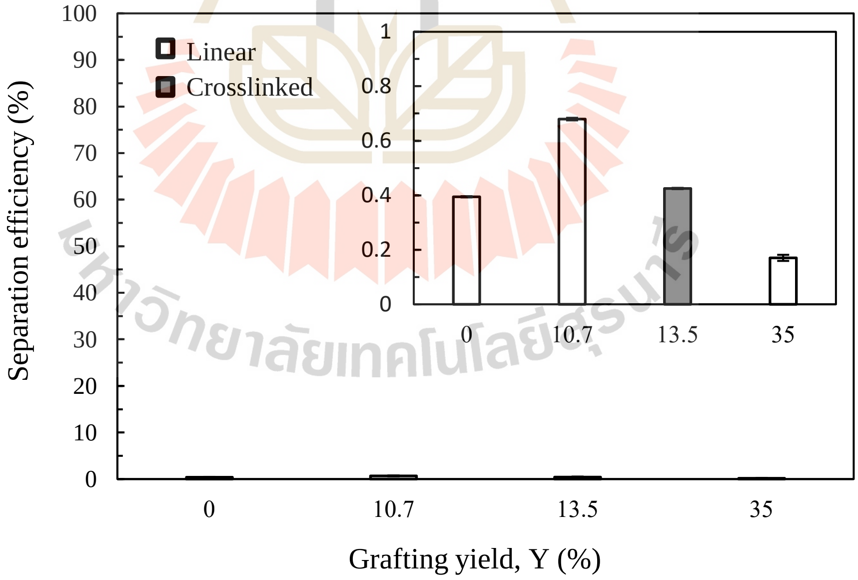


Figure 4.29 Separation efficiencies of PNIPAm grafted membrane with different grafting yield for separating water-in-paraffin oil at high temperature

4.5.2 Influence of PNIPAm structures on separation efficiency

The oil-in-water separation efficiency of the ungrafted Nylon membrane was considered approximately similar to that of the linear PNIPAm grafted membrane. This was attributed to the hydrophilicity of Nylon membrane. Thus, it could only separate oil-in-water emulsions at low temperature. With the same grafting yield, the separation efficiency of linear and crosslinked PNIPAm grafted membrane were almost the same (Figure 4.30). The separation efficiency of linear PNIPAm structure was 93%, while that of crosslinked PNIPAm structure was 94%. Therefore, this inferred that the effect of PNIPAm structures was independent of the oil-water emulsion separation.

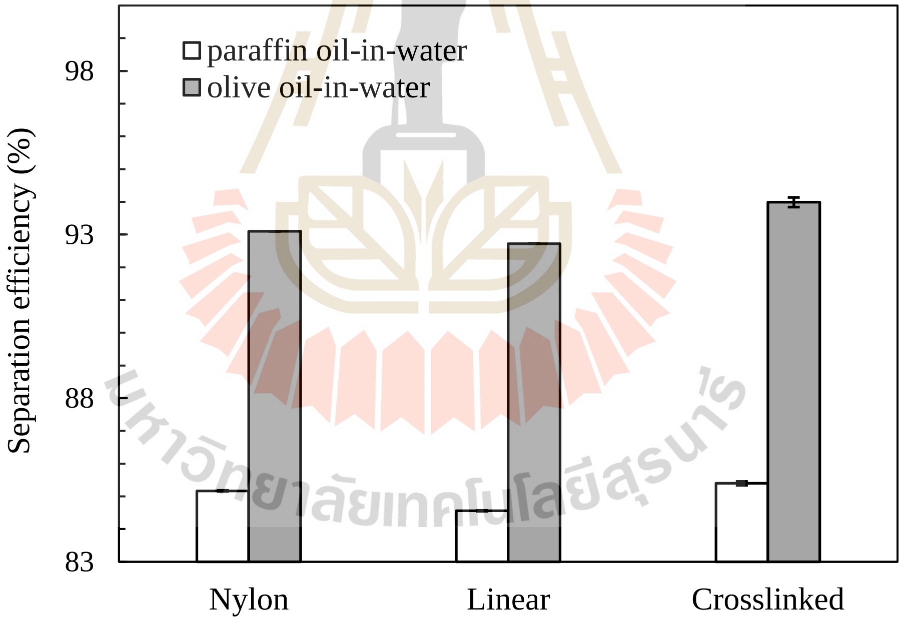


Figure 4.30 Separation efficiencies of grafted membrane with different PNIPAm structures for separating different oil-in-water emulsions at low temperature

CHAPTER V

CONCLUSIONS

Poly(*N*-isopropylacrylamide), PNIPAm was successfully grafted onto Nylon-6 porous membranes by using the novel synthesize technique. Plasma peroxide method coupled with microwave-assisted polymerization. FT-IR spectra of the grafted membrane demonstrated the transmission peak at wavenumber 2970 cm^{-1}, 1385 cm^{-1} and 1368 cm^{-1} which confirmed the success of grafting of PNIPAm. The optimization of plasma peroxide technique coupled with microwave-assisted polymerization method was determined by grafting yield and morphology of the membrane. The high grafting yield was obtained at temperature higher than 85°C from microwave-assisted polymerization. However, the grafted membranes were fractured when grafting with the temperature over than 90°C. SEM micrographs demonstrated that the grafted membranes were fractured when grafting with the irradiation time over 15 min under 800 w. This was because the bubble formation, from huge steam of superheated water in the microwave irradiation, damaged the membrane. The fractured membranes were unsuitable to be used for gating applications. Therefore, the PNIPAm grafted membranes should be fabricated at a proper irradiation time of 10 min and under a proper output power of 800 w to obtain the optimum grafting yield.

The grafted PNIPAm chains located mainly on the top surface and the pore entrance of the membranes. The coverage of grafted PNIPAm chains on the membrane was inhomogeneous distributed. However, the uniformity and thickness of grafted

PNIPAm on pores surface was improved after using a pressure-assisted permeation technique. When the grafting yield increased, the intensity of PNIPAm characteristics peaks from FT-IR spectra increased. The thickness of grafted PNIPAm onto membrane became denser. The grafted PNIPAm chains also formed inside the pores of the membrane as shown in SEM micrographs. Moreover, the decrease of the BET surface area confirmed the pore size of the membrane became smaller. With the same grafting yield, the linear PNIPAm structure which irregular form and discontinuity of chains attached to the top surface and pore entrance of the Nylon membrane. While the crosslinked structure looks like a flat thin sheet of PNIPAm network placed on the top surface of the Nylon membrane. The water contact angle on linear grafted PNIPAm responded to the temperature below (25°C) and above LCST (35°C) higher than crosslinked grafted PNIPAm and ungrafted membrane, respectively. As a result, the linear PNIPAm grafted membrane exhibited hydrophilic-hydrophobic switching in higher degree than crosslinked PNIPAm grafted membrane. At the temperature below LCST, the water contact angles of both grafted membranes decreased. When the temperature above LCST, the water contact angles of both grafted membranes increased. These demonstrated hydrophilic and hydrophobic behaviors of the grafted membrane at low and high temperatures, respectively. The thermo-responsive gating characteristics were achieved from water filtration experiments in two different flow modes. The feedwater at the temperature of 25-45°C was penetrated through the membranes in cross-flow and direct flow modes. In both of flow mode, the water flux of linear PNIPAm grafted Nylon membranes with proper grafting yields exhibited a sharp response around 32°C. At all feedwater temperatures, the water fluxes mostly decreased with the increase of grafting yield. This was due to the pore size decreased with increasing PNIPAm grafted on the inner pore surface and pore entrance. However, the pores being choked by too much linear grafted PNIPAm (*Y*=43.2%) and no longer acted as thermo-responsive gates effectively. The optimal grafting yield of the excellent thermo-responsive gating performance was 22-35% for linear PNIPAm grafted membrane in both of water flow modes. Compared with the crosslinked PNIPAm gate, the water flux slightly increased with the increasing of temperature. No sharp response was observed and the membrane did not effectively act as thermo-responsive gates. However, the water flux at all temperature decreased with the grafting yield increased. The pores being choked by too much crosslinked grafted PNIPAm at critical grafting yield of 8.93% and 92.7% in cross flow and direct flow modes, respectively. The optimum grafting yield for high thermo-responsive gating characteristic in both of water flow mode was 21-92% for crosslinked PNIPAm grafted membrane. At the same grafting yield, linear PNIPAm grafted Nylon membranes exhibited much higher thermo-responsive gating coefficients (R) than the crosslinked PNIPAm grafted Nylon membranes. The gating performance of linear PNIPAm grafted membrane was better than that of crosslinked PNIPAm grafted membrane. The stability of the grafted PNIPAm gates in the membrane pores in long-term operations indicated by the reversibility and the repeatability. The temperature of feedwater was controlled by heated up from 25°C to 40°C and cooled down from 40°C to 25°C as a cycle. Within 10 runs, both grafted PNIPAm gates exhibited stable gating characteristics in direct flow mode. On the other hand, linear and crosslinked PNIPAm grafted membranes exhibited unstable gating characteristics in cross flow mode. The water flux decreased in every single cycle, and became zero in the crosslinked grafted membrane. Only the linear PNIPAm grafted membrane exhibited repeatability of thermo-responsive open-close gating switch within 10 runs. However, the linear PNIPAm grafted membrane showed irreversibility within 10 runs. Hence, reversibility and repeatability of thermo-responsive open-close gating switch depended on the water flow mode in the experiment. The prolonged experiment in high operating pressure, cross flow mode, could facilitate the disengagement leading to the plastic deformation in the PNIPAm resulting in irreversibility of the gates. Consequently, the linear PNIPAm grafted membrane achieved the reversible and repeatable thermo-responsive open-close switch performance within 10 runs of operation under 100 kPa in direct flow mode.

In the thermo-responsive gating application, the PNIPAm grafted Nylon membrane with switchable hydrophilicity and hydrophobicity was excellently separate oil-in-water emulsions. Comparing the grafting yield and the chain structure, the grafting yield was the dominant factor influencing the separation process. The oil-in-water emulsion was separated at low temperature for the hydrophilic membrane. The water-in-oil emulsion was separated at high temperature for the hydrophobic membrane. An increase of grafting yield resulted in an improvement in the separation efficiency of oil-water emulsion. At the same grafting yield, the linear and crosslinked PNIPAm grafted membranes could separate oil-in-water emulsions with high efficiency. The linear PNIPAm grafted Nylon membrane with 35.7% of grafting yield could separate olive oil-water emulsion at low temperature (25°C) with a very high separation efficiency of ≥99.7%. In case of water in oil emulsions, the grafted PNIPAm membrane could only separate water-in-paraffin oil with poor efficiency. This was attributed to the effect of density between water and oil. Since density of oil was lower than that of water, oil floated on top of the water. Thus, oil was blocked when the hydrophobic surface of the membrane was covered by water.

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APPENDIX A

PREPARATION OF DPPH STANDARD SOLUTION

Chemical:

- 2,2-Diphenyl-1-picrylhydrazyl (DPPH) ($C_{18}H_{12}N_5O_6$, Sigma-Aldrich; St. Louis, USA)
- Benzene (Loba-AR grade, Bombay)

Preparation:

2,2-Diphenyl-1-picrylhydrazyl (DPPH) solution (33.4 mg/L): 0.0033 g of DPPH was dissolved with benzene and made up to 100 ml of final volume and stored at room temperature.

Reagents:

1. concentrate solution : 200 mg/l of DPPH in Benzene

Dissolved 0.45 mg of DPPH in Benzene and made up to 2.25 ml of final volume.

2. standard DPPH solution (2, 4, 6, 8, 10, and 15 mg/l respectively)

- Dilute concentrate solution 0.1 ml in Benzene with made up to 10 ml of final volume.

- Dilute concentrate solution 0.2 ml in Benzene with made up to 10 ml of final volume.

- Dilute concentrate solution 0.3 ml in Benzene with made up to 10 ml of final volume.

- Dilute concentrate solution 0.4 ml in Benzene with made up to 10 ml of final volume.

- Dilute concentrate solution 0.5 ml in Benzene with made up to 10 ml of final volume.

- Dilute concentrate solution 0.75 ml in Benzene with made up to 10 ml of final volume.

APPENDIX B

CALCULATION OF PEROXIDE CONCENTRATION

Calculation :

1. DPPH concentration which remained after the reaction was obtained from UV-Vis.

2. The reacted DPPH concentration was obtained by using the following equation :

reacted DPPH concentration = DPPH concentration (before reaction) - DPPH concentration (after reaction)

Defined : DPPH concentration (before reaction) = 33.4 mg/l

3. Peroxide concentration was obtained by using the following equation :

Peroxide concentration = reacted DPPH concentration /2

Note : The peroxide concentration was evaluated using a method developed by Piao et al., which estimated the peroxide concentration as half the amount of DPPH reacted.

Calibration curve of DPPH concentration

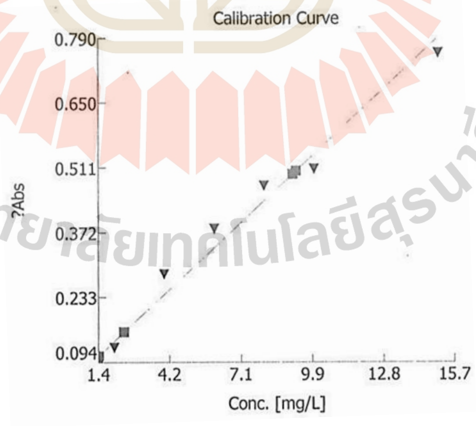


Figure A.1 calibration curve of DPPH concentration

Order of curve: 1st

Equation: Conc = K1*(Abs) + K0

Calibration method: Concentratior

K0: -0.7648

K1: 19.91588

R: 0.9892

Repetition: 3

Zero interceept: Yes

Black: Yes

Measure wavelength: 521 nm

Table A.1 Results of calibration curve of DPPH concentration

No.	Conc (mg/l)	Abs
1	2	0.125
2	4	0.283
3	6	0.381
4	8	0.472
5	10	0.509
6	15	0.758

Table A.2 Results of peroxide concentration

conditon	Abs	Conc(mg/L)	Conc_reacted	**peroxide**	g/l	mol/l	mol/cm^3
normal_1	0.104	1.3	32.1	16.05	0.01605	4.07E-05	4.07E-08
normal_2	0.107	1.4	32	16	0.016	4.06E-05	4.06E-08
20w_1	0.158	2.4	31	15.5	0.0155	3.93E-05	3.93E-08
20w_2	0.094	1.1	32.3	16.15	0.01615	4.10E-05	4.10E-08
40w_1	0.070	0.6	32.8	16.4	0.0164	4.16E-05	4.16E-08
40w_2	0.058	0.4	33	16.5	0.0165	4.18E-05	4.18E-08
15sccm_1	0.059	0.4	33	16.5	0.0165	4.18E-05	4.18E-08
15sccm_2	0.058	0.4	33	16.5	0.0165	4.18E-05	4.18E-08
2min_1	0.055	0.3	33.1	16.55	0.01655	4.20E-05	4.20E-08
2min_2	0.055	0.3	33.1	16.55	0.01655	4.20E-05	4.20E-08

APPENDIX C

CALCULATION OF WATER FLUX

1. Measure the time of sufficient water permeation through the membrane.

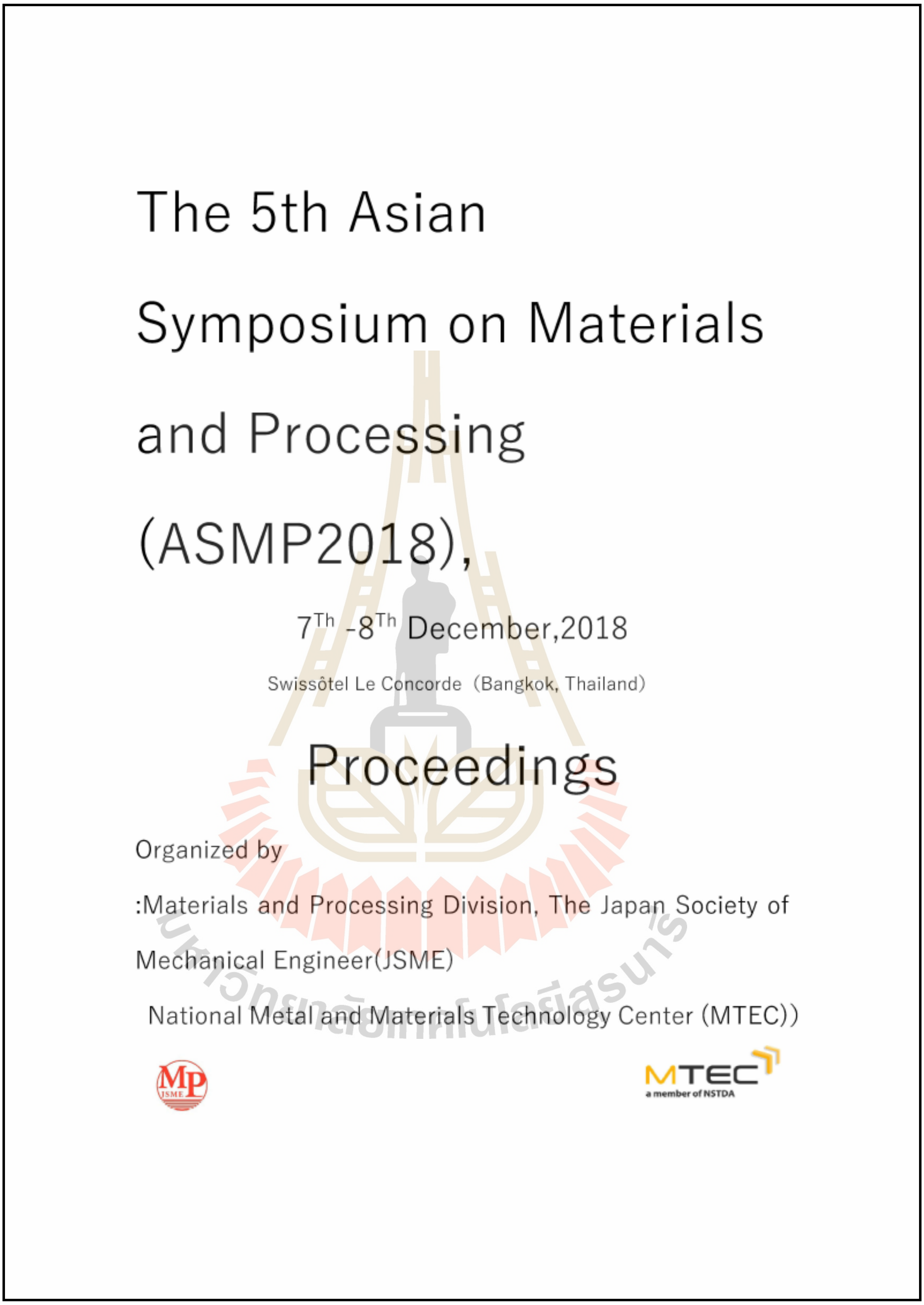
2. Water flux was obtained by using the following equation:

Water flux = among of permeated water / (time x membrane area)

Defined : membrane area of permeation = 11.34 cm^2 (diameter = 38 mm)

APPENDIX D

LIST OF PUBLICATIONS



The 5th Asian Symposium on Materials and Processing (ASMP2018),

7Th -8Th December,2018

Swissôtel Le Concorde（Bangkok, Thailand）

Proceedings

Organized by

:Materials and Processing Division, The Japan Society of Mechanical Engineer(JSME)

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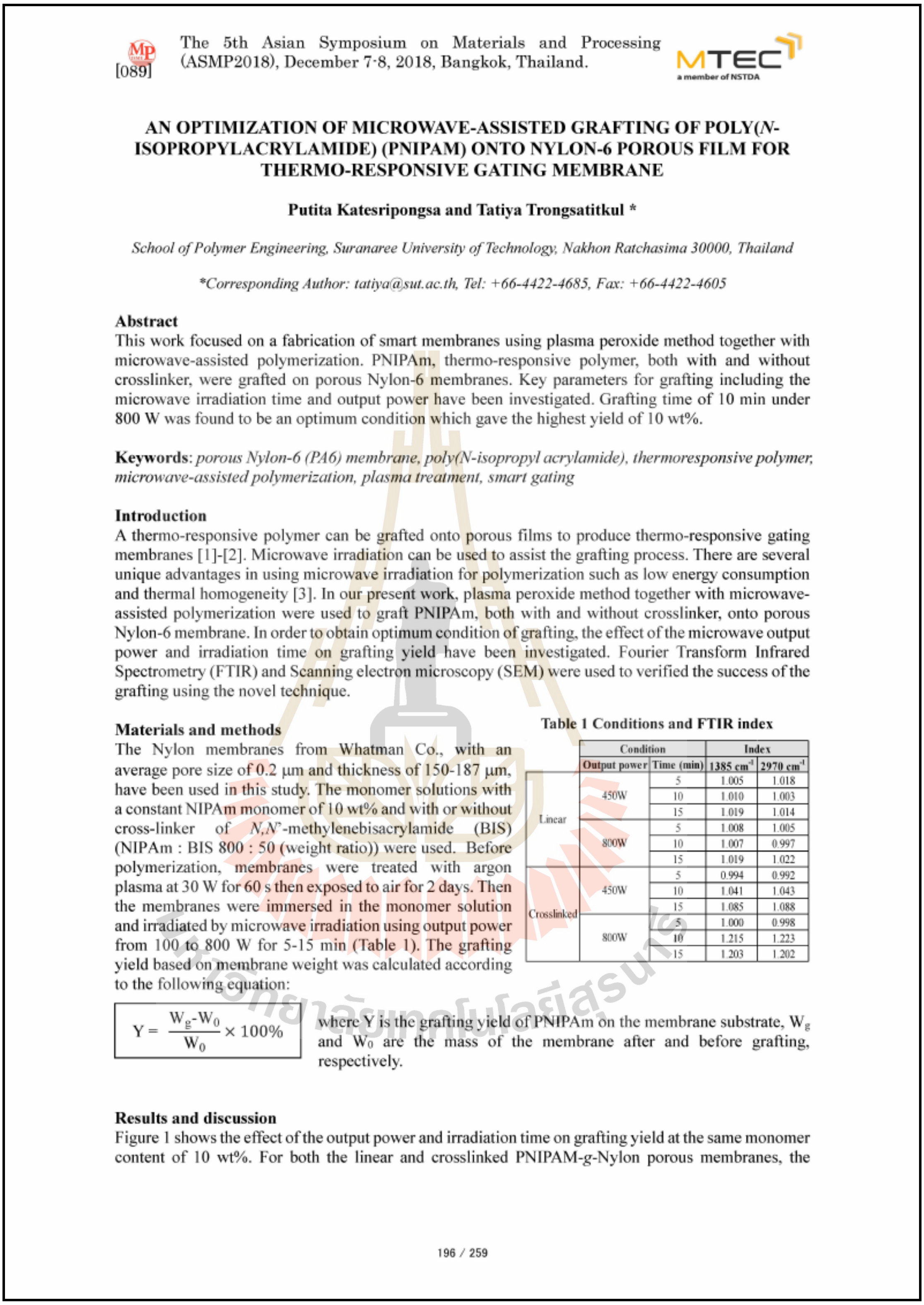

[089] The 5th Asian Symposium on Materials and Processing (ASMP2018), December 7-8, 2018, Bangkok, Thailand.
MTEC a member of NSTDA

AN OPTIMIZATION OF MICROWAVE-ASSISTED GRAFTING OF POLY(*N*-ISOPROPYLACRYLAMIDE) (PNIPAM) ONTO NYLON-6 POROUS FILM FOR THERMO-RESPONSIVE GATING MEMBRANE

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Abstract

This work focused on a fabrication of smart membranes using plasma peroxide method together with microwave-assisted polymerization. PNIPAm, thermo-responsive polymer, both with and without crosslinker, were grafted on porous Nylon-6 membranes. Key parameters for grafting including the microwave irradiation time and output power have been investigated. Grafting time of 10 min under 800 W was found to be an optimum condition which gave the highest yield of 10 wt%.

Keywords: *porous Nylon-6 (PA6) membrane, poly(N-isopropyl acrylamide), thermoresponsive polymer, microwave-assisted polymerization, plasma treatment, smart gating*

Introduction

A thermo-responsive polymer can be grafted onto porous films to produce thermo-responsive gating membranes [1]-[2]. Microwave irradiation can be used to assist the grafting process. There are several unique advantages in using microwave irradiation for polymerization such as low energy consumption and thermal homogeneity [3]. In our present work, plasma peroxide method together with microwave-assisted polymerization were used to graft PNIPAm, both with and without crosslinker, onto porous Nylon-6 membrane. In order to obtain optimum condition of grafting, the effect of the microwave output power and irradiation time on grafting yield have been investigated. Fourier Transform Infrared Spectrometry (FTIR) and Scanning electron microscopy (SEM) were used to verified the success of the grafting using the novel technique.

Materials and methods

The Nylon membranes from Whatman Co., with an average pore size of 0.2 μm and thickness of 150-187 μm, have been used in this study. The monomer solutions with a constant NIPAm monomer of 10 wt% and with or without cross-linker of *N,N'*-methylenebisacrylamide (BIS) (NIPAm : BIS 800 : 50 (weight ratio)) were used. Before polymerization, membranes were treated with argon plasma at 30 W for 60 s then exposed to air for 2 days. Then the membranes were immersed in the monomer solution and irradiated by microwave irradiation using output power from 100 to 800 W for 5-15 min (Table 1). The grafting yield based on membrane weight was calculated according to the following equation:

Table 1 Conditions and FTIR index

	Condition		Index	
	Output power	Time (min)	1385 cm^{-1}	2970 cm^{-1}
Linear	450W	5	1.005	1.018
		10	1.010	1.003
		15	1.019	1.014
	800W	5	1.008	1.005
		10	1.007	0.997
		15	1.019	1.022
Crosslinked	450W	5	0.994	0.992
		10	1.041	1.043
		15	1.085	1.088
	800W	5	1.000	0.998
		10	1.215	1.223
		15	1.203	1.202

$$\boxed{Y = \frac{W_g - W_0}{W_0} \times 100\%}$$

where Y is the grafting yield of PNIPAm on the membrane substrate, W_g and W_0 are the mass of the membrane after and before grafting, respectively.

Results and discussion

Figure 1 shows the effect of the output power and irradiation time on grafting yield at the same monomer content of 10 wt%. For both the linear and crosslinked PNIPAM-g-Nylon porous membranes, the

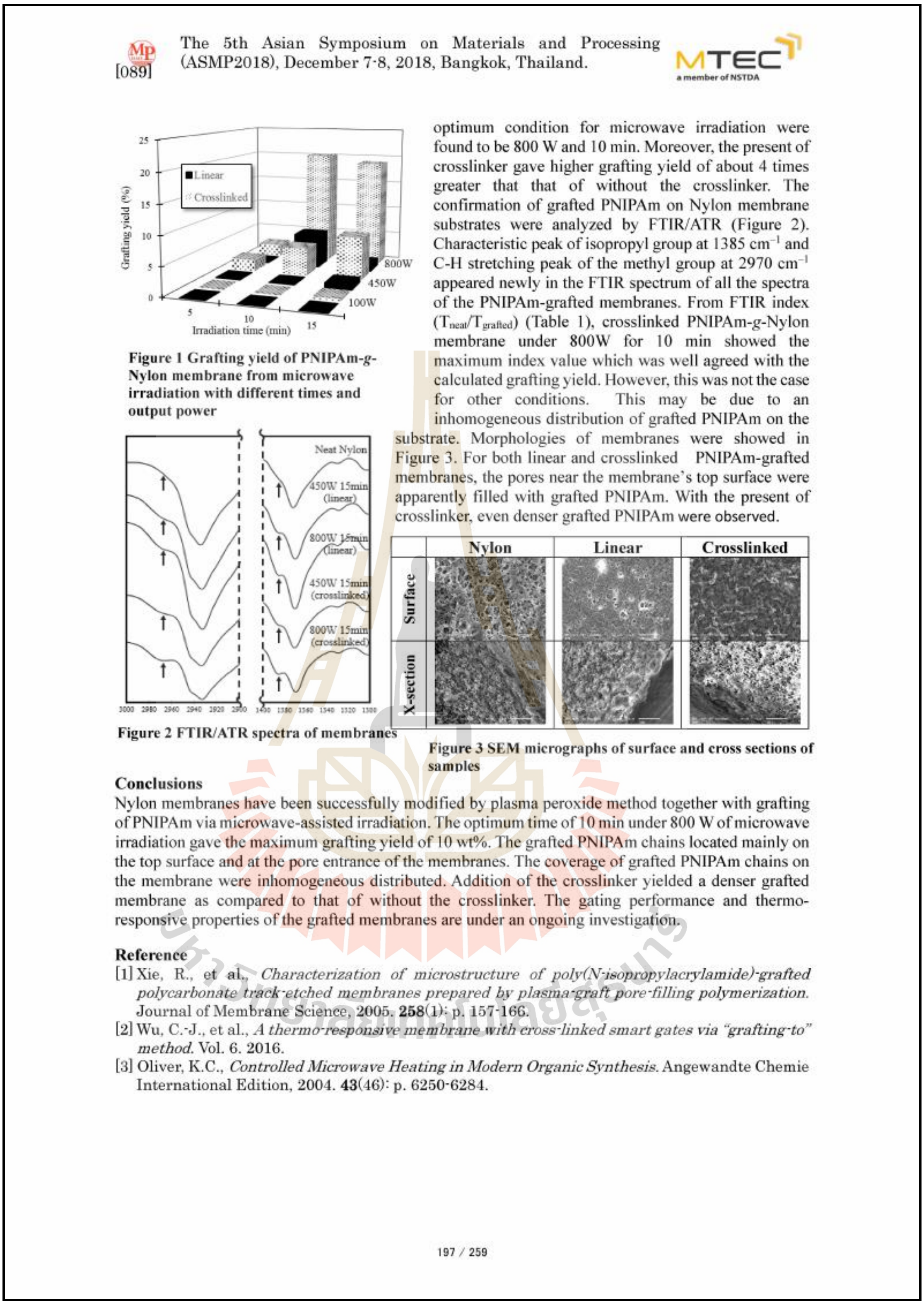

Figure 1 Grafting yield of PNIPAm-*g*-Nylon membrane from microwave irradiation with different times and output power

Figure 2 FTIR/ATR spectra of membranes

optimum condition for microwave irradiation were found to be 800 W and 10 min. Moreover, the present of crosslinker gave higher grafting yield of about 4 times greater that that of without the crosslinker. The confirmation of grafted PNIPAm on Nylon membrane substrates were analyzed by FTIR/ATR (Figure 2). Characteristic peak of isopropyl group at 1385 cm^{-1} and C-H stretching peak of the methyl group at 2970 cm^{-1} appeared newly in the FTIR spectrum of all the spectra of the PNIPAm-grafted membranes. From FTIR index ($T_{neat}/T_{grafted}$) (Table 1), crosslinked PNIPAm-*g*-Nylon membrane under 800W for 10 min showed the maximum index value which was well agreed with the calculated grafting yield. However, this was not the case for other conditions. This may be due to an inhomogeneous distribution of grafted PNIPAm on the substrate. Morphologies of membranes were showed in Figure 3. For both linear and crosslinked PNIPAm-grafted membranes, the pores near the membrane's top surface were apparently filled with grafted PNIPAm. With the present of crosslinker, even denser grafted PNIPAm were observed.

Figure 3 SEM micrographs of surface and cross sections of samples

Conclusions

Nylon membranes have been successfully modified by plasma peroxide method together with grafting of PNIPAm via microwave-assisted irradiation. The optimum time of 10 min under 800 W of microwave irradiation gave the maximum grafting yield of 10 wt%. The grafted PNIPAm chains located mainly on the top surface and at the pore entrance of the membranes. The coverage of grafted PNIPAm chains on the membrane were inhomogeneous distributed. Addition of the crosslinker yielded a denser grafted membrane as compared to that of without the crosslinker. The gating performance and thermo-responsive properties of the grafted membranes are under an ongoing investigation.

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An optimization of microwave-assisted grafting of poly(*N*-isopropylacrylamide) (PNIPAM) onto nylon-6 porous film for thermo-responsive gating membrane

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Abstract

This work focused on a fabrication of smart membranes using a novel grafting method comprising of plasma peroxide technique together with microwave-assisted polymerization. PNIPAm, thermo-responsive polymer, both with and without crosslinker, were grafted onto porous Nylon-6 membranes. Key parameters for grafting including the microwave irradiation time, output power, and monomer concentration have been investigated. Characterizations using scanning electron microscope (SEM) and Fourier-transform infrared spectroscopy (FTIR) revealed that the PNIPAm have been successfully grafted onto the surface both on the top surface of the membrane and the surface inside the pores. Irradiation time of 10 min under 800 w were found to be an optimum condition which gave the highest yield of 10 wt%. For both the linear and crosslinked PNIPAm-grafted membranes, the highest grafting yield was obtained from using 3 wt% of NIPAm monomer solution. Because of this fast fabrication time and environmentally friendly method, new smart gating membranes can be produced which will help providing an ever-better performances transport control of gas and liquid for various fields including medical and packaging applications.

Keywords : Porous nylon-6 (PA6) membrane, Poly(*N*-isopropylacrylamide), Thermoresponsive polymer, Microwave-assisted polymerization, Plasma treatment, Smart gating

1. Introduction

Smart polymers or stimuli-responsive polymers are polymers that respond with a considerable change in their properties to different stimuli or changes in the environment. This type of polymer may be classified according to the stimuli it responds to including temperature, pH, photo, or enzyme. Poly(*N*-isopropylacrylamide) or PNIPAm is a smart polymer which has been extensively studied. This is because PNIPAm is a thermo-responsive polymer that possesses a well-defined lower critical solution temperature or LCST at around 32°C (Xie et al., 2007). This temperature is useful as it is close to physiological temperature which can also be adjusted or tailored by copolymerization with another monomer (Trongsatitkul and Budhlall, 2011). This is the main reason that most researchers focus to exploit PNIPAm in medical field such as controlled release (Chung - Yang et al., 2009), tissue engineering (Stile and Healy, 2001), and immobilization of enzymes (Liu et al., 2012).

Another use of PNIPAm that has been attracting wide interests over the last decade is a smart gating application. In this case, permeation properties can be controlled or adjusted by the gates according to an environmental temperature. To be specific, PNIPAm chains are attached or graft onto a porous membrane's surface. Collapses of PNIPAm chains as temperature increases above the LCST are exploited as an open/close mechanism of the pores or gates on the membrane. Several applications could find these smart gating membranes advantageous including controlled drug delivery, bio-separation, chemical separation, water treatment, chemical sensors, and tissue engineering.

Different applications require different gating performance. It has been shown that linear chain PNIPAm generally

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gives a sharp response to temperature change (Schild, 1992). However, a three-dimensional crosslink network of PNIPAm may be better in term of open/close gating performance (Chen et al., 2009).

Beside the form of grafted PNIPAm on the membrane surface, type of substrate used also affects gating performance. Many stimuli-responsive gating membranes have been investigated such as PNIPAm-*g*-Nylon-6 (Yang et al., 2006), PNIPAm-*g*-PP (Choi et al., 2000), PNIPAm-*g*-PVDF (Yang et al., 2006), PNIPAm-*g*-PC (Ohashi et al., 2016), and PNIPAm-*g*-HDPE (Yamaguchi et al., 1999) membranes. Comparative study of smart gating membranes with different substrates on gating performance were carried out by Yang et al.(2006). By measuring the water flux over the temperature range of 25-40°C, it was found that the water flux through the hydrophilic Nylon-6 substrate was higher than that of through the hydrophobic HDPE substrate at the same temperature (Yang et al., 2006) which was due to the differences in the substrate properties, specifically its hydrophilicity and microstructure.

Several grafting techniques have been developed to graft PNIPAm onto a membrane such as plasma induced graft polymerization (PIGP) (CHU Liangyin, 2003), UV radiation induced grafting, plasma graft copolymerization, atom transfer radical polymerization (ATRP) (Xu et al., 2007), and plasma-graft pore-filling polymerization (Xie et al., 2005). Microwave irradiation can also be used to assist the grafting process. There are several unique advantages in using microwave irradiation for polymerization including low energy consumption and thermal homogeneity (Oliver, 2004). Earlier work reported a successful use of microwave-assisted heating for synthesize PNIPAm hydrogels which shortened the reaction time of 6 h down to 1 h (Murray et al., 1994). However, to the best of the authors' knowledge, the microwave-assisted grafting technique of PNIPAm onto Nylon porous membrane has not been investigated.

In this study, plasma peroxide method together with microwave-assisted polymerization were used to graft PNIPAm, onto a porous Nylon-6 membrane. This was because Nylon membrane was hydrophilic which featured porous honeycomb microstructure below the skin layer that can be effectively grafted with PNIPAm and exhibited a high gating performance. The focus of this work was to optimize the key parameters involving with microwave-assisted grafting. These key parameters included the effect of the microwave output power and irradiation time as well as concentration of the monomer solution on grafting yield. The presence of crosslinker in the monomer solution was also investigated for its effects on the grafting yield and, to be reported later (elsewhere), gating performance. Fourier transform infrared spectrometry (FTIR) and scanning electron microscopy (SEM) were used to verify the success of the grafting using the novel technique.

2. Experimental methods

2.1 Materials

The Nylon membranes used in this study were from Whatman Co. They possessed an average pore size of 0.2 µm and thickness of 150-187 µm. *N*-isopropylacrylamide (NIPAm) (98%) and *N, N'*-methylenebisacrylamide (BIS), used as the main monomer and a crosslinker, respectively and were purchased from TCI Co. The monomer and crosslinker were used without further purification. Deionized water was used in all experiment throughout the study.

2.2 Grafting of linear and crosslinked PNIPAm onto porous nylon 6 substrates by plasma peroxide method together with microwave-assisted polymerization

The mechanism for grafting PNIPAm onto nylon porous membrane surfaces is schematically depicted as shown in Fig. 1.

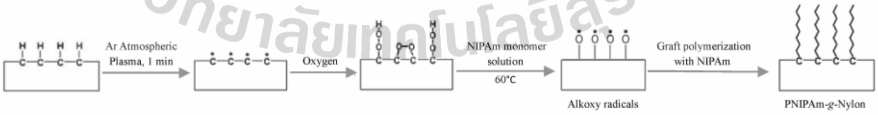

Fig. 1 Grafting of NIPAm onto Nylon-6 porous membrane's surface via plasma peroxide method followed by microwave-assisted polymerization.

Firstly, as-received Nylon 6 membranes were treated with argon plasma at 30 W for 60 s to activate the surface of the polymer membranes and to form free radicals. These activated membranes were then exposed to oxygen in the atmospheric air for 2 days so that the free radicals reacted with oxygen and formed hydrogen peroxide on the membrane's surface. All the parameters in the first step were kept constant.

Secondly, NIPAm monomers were grafted onto the membrane's surface using microwave-assisted polymerization. In this step, the treated membranes were submerged in NIPAm monomer solution before being irradiated with microwave to induce grafting polymerization by heating. Typically, as the peroxides being the assumed initiator, the applied grafting temperature is normally higher than 60°C to assure the decomposition of peroxides to produce alkoxy radicals in aqueous solution, thereby initiating the polymerization (Xueqin et al., 2014). Effects of the main parameters in the second step i.e. microwave irradiation output power and time, the presence of crosslinker, and the concentration of the monomer concentration on the grafting effectiveness or grafting yield were examined. Optimum condition for grafting of PNIPAm onto the porous Nylon membrane was expected to obtain from this investigation. The optimization of microwave assisted polymerization step was carried out as followed.

1. To study effect of microwave irradiation *output power* and *time,* the monomer solution comprised of 10 wt% NIPAm in water was used. A treated membrane was fully submerged into the monomer solution in a Petri dish. Irradiation of microwave power and time were varied from 100 to 800 w and 5 to 15 min, respectively. After completion of microwave irradiation step. The grafted membrane was repeatedly rinsed with DI water before mildly sonicated in a temperature-controlled bath (30°C) for 24 h to ensure the removal of any residual unreacted chemicals. Finally, the grafted membrane was dried in an oven at 50°C for 12 h before being tested or characterized.
2. The study of the effects of the *presence of BIS crosslinker* and *the monomer solution concentration* were performed by using the optimum microwave irradiation condition obtained from the prior step. The monomer solutions, with and without crosslinker, with a constant solid content were prepared. In the case of the solution with the presence of crosslinker, the constant weight ratio of 800:50 (NIPAm:BIS) was used. The monomer solution concentrations varied from 2 to 10 wt% were prepared. The grafting of the treated membranes with the different monomer solutions were carried out as described above. Different conditions used for optimization in this study were summarized in Table 1.

Table 1 Conditions for the PNIPAm-*g*-Nylon membranes.

Condition no.	NIPAm (wt%)	Output power (w)	Irradiation time (min)
1	10	100	5
2			10
3			15
4		450	5
5			10
6			15
7		800	5
8			10
9			15
10	7	Optimum condition	
11	5		
12	3		
13	2		

The grafted membranes obtained from the different compositions were characterized for their grafting effectiveness via FTIR, SEM, and weighing method for the proof of reaction, change in structure, and grafting yield, respectively. The grafting yield based on membrane weight was calculated according to the following Eq. (1).

$$Y = \frac{W_g - W_0}{W_0} \times 100\% \tag{1}$$

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where Y is the grafting yield of PNIPAm on the membrane substrate, W_g and W_0 are the mass of the membrane after and before grafting, respectively (Yang et al., 2006).

2.3 Morphological analysis

Scanning electron microscopy (SEM) (JSM-6010LV, JEOL, Japan) was employed to observe the microstructures of the membranes, both outer surface and cross-sectional area. The cross-sectional area of the membranes were prepared by cryo-fractured in liquid nitrogen. All the surfaces were sputter-coated with gold for 60 s before observation with SEM at an accelerating voltage of 10 kV.

2.4 Chemical composition analysis

Fourier Transform Infrared Spectrometer (FT-IR) (Tensor 27, Bruker, Billerica, MA, USA) was used to confirm the grafting of PNIPAm polymer onto the Nylon 6 porous membranes. The attenuated total reflection (ATR) mode was used for all the samples. The spectra were collected at 4 cm^{-1} resolution with an FT-IR microscopic spectrometer over 64 scans.

3. Results and discussion

3.1 Confirmation of grafted PNIPAm on nylon membranes

The effects of microwave irradiation time and output power on the success of grafting of PNIPAm onto Nylon-6 porous membranes were first investigated. The results shown in Fig. 2 illustrated the effect of the output power and irradiation time on grafting yield at a constant monomer content of 10 wt%. It can be seen that PNIPAm-*g*-Nylon membranes with a grafting yield of 2.85-11.2 % and 11.7-18.3 % were obtained for linear and crosslinked PNIPAm-grafted membranes, respectively. For both the linear and crosslinked PNIPAM-*g*-Nylon porous membranes, the condition for microwave irradiation that gave the highest yield were found to be 800 W and 10 min. Note that, with the presence of crosslinker in the monomer solution, grafting yield was about 4 times greater than that of without one.

Different yields obtained from the use of different microwave irradiation time and power during microwave-assisted polymerization were due to the different temperatures were induced. In this Novel grafting method, temperature of 60°C or above is required to produce alkoxy radicals from peroxides. Figure 3 shows the temperatures measured on the surface of Nylon using IR thermosensor immediately after microwave irradiation. The temperatures of the membranes were varied from 44 to 92°C. It should be noted that due to the time lag of the temperature measurement, the actual temperature during the irradiation may be significantly higher than these value. In general, however, it can be seen that higher temperature and longer time gave higher yield. The results infer that the grafting yield is time and temperature dependent. However, there seemed to be the limiting or critical temperature at 87°C that gave the maximum yields. Further increased the grafting temperature resulted in declining of the grafting yield. This result is similar to that of reported by Xueqin et al.(2014). In general, a decrease in grafting yield at elevated temperature is known and accepted as a consequence of an acceleration of the termination reaction. The increased temperature causes faster rates of peroxide decomposition, free radical consumption, and termination.

Regarding of the grafting temperature, it should also be noted that all conditions used here induced temperature significantly higher than the LCST of NIPAm (32°C). Thus, during the grafting process, PNIPAm chains were assumed to aggregate in all conditions. The aggregation of the polymer chains may partially be responsible for low grafting yield, particularly in the case when a high monomer concentration solution was used. However, the yield obtained in this study at low concentration such as at 3 wt% was comparable to that of reported by others (Yang et al., 2006). This might plausibly be due to that the pores were pre-filled with enough amount of monomer within. The aggregation of the polymer ,that could have prevented the permeation of monomer molecules from solution outside the pore, therefore show no effect on the grafting yield. This was only the case for monomer solution with low concentration, but not for the higher concentration one. The effect of monomer concentration is discussed in this report in the later section.

The success of grafting using the novel technique was confirmed by ATR-FTIR technique shown in Fig. 4.

Characteristic peak of isopropyl group at 1385 cm^{-1} appeared newly in the spectra of the PNIPAm-grafted membranes which prepared using microwave irradiation at 450 w for 15 min and 800 w for 10 and 15 min. From FTIR spectra, FTIR index ($T_{neat}/T_{grafted}$) was calculated and summarized in Table 2. The maximum index value was observed in the grafted sample prepared under 800 w for 10 min with the presence of crosslinker. The result was well agreed with the calculated grafting yield. However, this was not the case for other conditions. This might be due to an inhomogeneous distribution of grafted PNIPAm on the substrate.

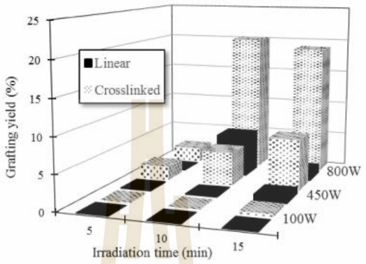

Fig. 2 Grafting yield of PNIPAm-*g*-Nylon membrane using different microwave irradiation time and output power with a constant 10 wt% NIPAm solution.

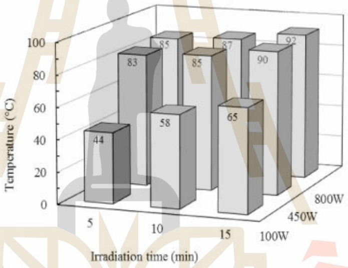

Fig. 3 Temperature of Nylon membrane at different microwave irradiation time and output power. (measure by infrared thermometer)

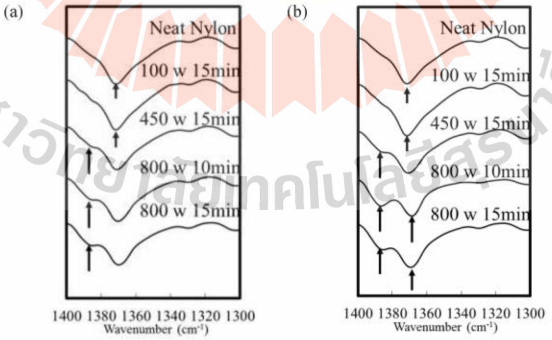

Fig. 4 FTIR/ATR spectra of membranes: (a) linear, and (b) crosslinked PNIPAm-*g*-Nylon membrane.

Table 2 FTIR index of membranes for grafting optimization.

	Condition		Index
	Output power (w)	Time (min)	1385 cm^{-1}
Linear	450	5	1.005
		10	1.010
		15	1.019
	800	5	1.008
		10	1.007
		15	1.019
Crosslinked	450	5	0.994
		10	1.041
		15	1.085
	800	5	1.000
		10	1.215
		15	1.203

The relationship between the grafting yield and NIPAm concentration is shown in Fig. 5. For both the linear and crosslinked PNIPAm-grafted membranes, the highest grafting yield was obtained from using 3 wt% of NIPAm monomer solution. Further increased PNIPAm concentration above 3 wt% gave lower yield suggesting that 3 wt% was a critical concentration to obtain highest degree of grafting. The plausible explanation was to be explained in the following section that reported about morphology of the grafted membrane.

It was again observed that the presence of crosslinker gave higher grafting yield than that of without one. Characteristic peak of isopropyl group at 1385 cm^{-1} appeared in the FTIR spectrum for grafted samples both linear (without crosslinker) and crosslinked PNIPAm-grafted membranes as shown in Fig. 6.

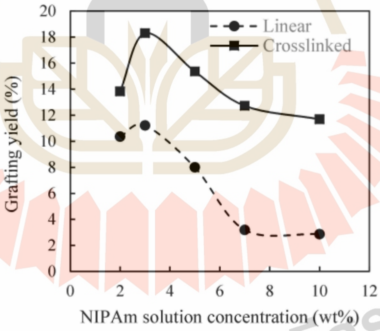

Fig. 5 Relationship between the NIPAm monomer solution concentration and the grafting yield onto Nylon-6 porous membrane.

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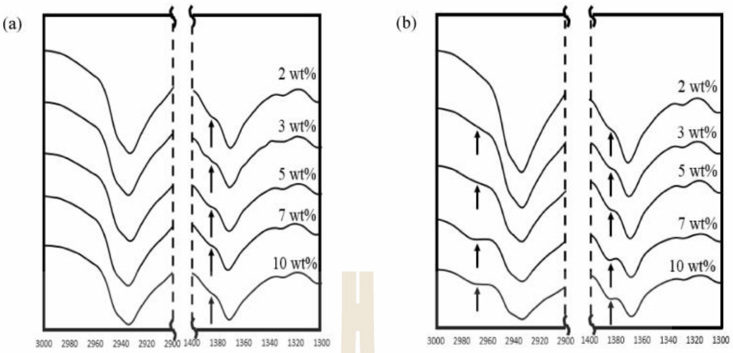

Fig. 6 FTIR/ATR spectra of Nylon-6 porous membranes grafted with: (a) linear, and (b) crosslinked PNIPAm using different monomer concentrations.

3.2 Morphological analysis of PNIPAm-grafted membranes

Morphologies of the grafted membranes were analyzed using SEM. SEM micrographs shown in Fig. 7 were a cryo-freeze fractured cross-section surface of the grafted membranes. It was described earlier that initially, the membrane was only immersed in the monomer solution before being irradiated with microwave, which result in a dense PNIPAm grafted mostly onto top surface of membrane. Attempting to improve grafting homogeneity, a pressure-assisted permeation of monomer solution was carried out. Adaptation of coffee maker "Aeropress" was employed to help forcing monomer solution to penetrate into the pores of the membrane. An improvement of grafting was observed as better uniformity of grafting of PNIPAm onto the porous Nylon was found and PNIPAm grafted onto the surface of deeper pores.

Morphologies of grafted membranes were shown in Fig. 8. For both linear and crosslinked PNIPAm-grafted membranes, the pores near the top surface of membrane were apparently filled with grafted PNIPAm. With the presence of crosslinker, even denser grafted PNIPAm were observed. It should be noted that under 800 w of microwave irradiation, when irradiation time was longer than 15 min, the membrane fracture was observed as shown in Fig. 9. This was suspected to be caused by the temperature in the microwave was higher than the service temperature of Nylon membrane. This irradiation that caused Nylon membrane fracture was thought to be the upper limit of grafting of Nylon membrane with PNIPAm. Thus, the optimum condition for microwave irradiation were found to be 800 W and 10 min for both the linear and crosslinked PNIPAM grafted on to Nylon porous membranes. For grafted membranes with different monomer concentration, a plausible explanation was that the higher concentration of monomer used, the denser grafting was being generated, especially on the top surface, and this prevented the NIPAM monomer in solution to diffuse into the pore of membrane as shown in Fig. 10. Therefore, the membrane was found to possess highly PNIPAm grafted on the top of surface which explain the increase of PNIPAm signal in FTIR and not in grafting yield that calculated by weight.

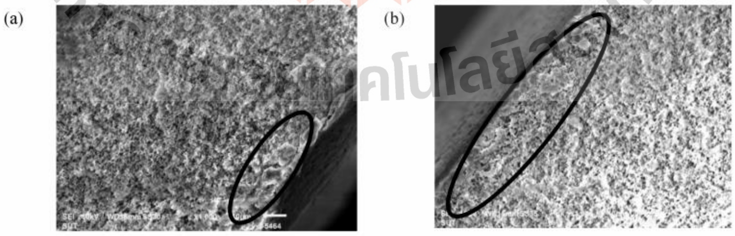

Fig. 7 SEM micrographs of cross sections of grafted samples: (a) without pressure assisted, and (b) with pressure assisted.

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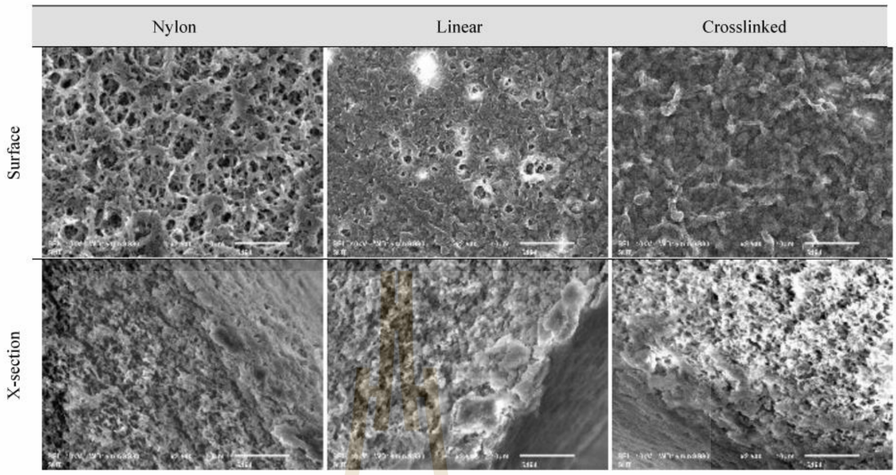

Fig. 8 SEM micrographs of surface and cross sections of samples.

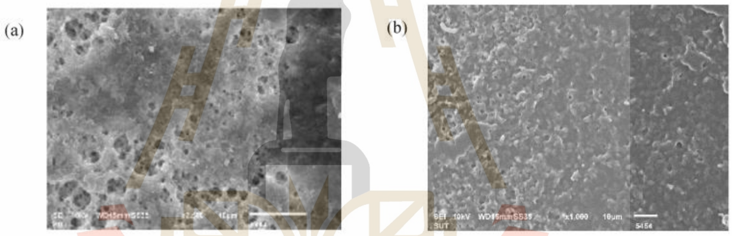

Fig. 9 SEM micrographs of a fractured microstructure of PNIPAm grafted membranes (surface) (a) 800W 30 min (linear) and (b) 800W 15 min (crosslinked)

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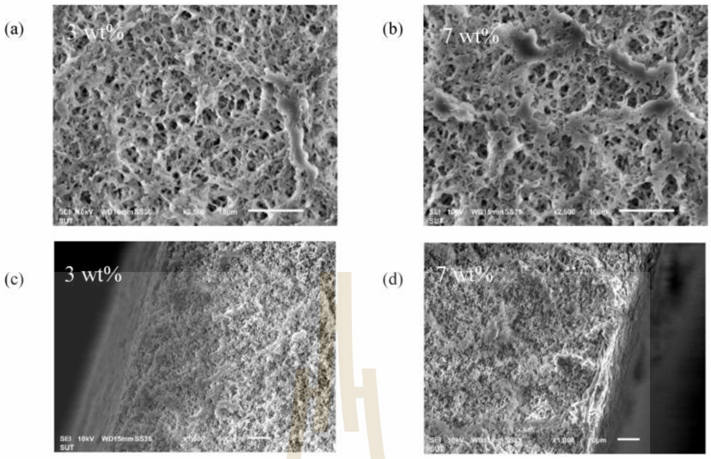

Fig. 10 SEM micrographs of samples: surface of grafted membrane with (a) 3 wt%, (b) 7 wt%, and cross-section of grafted membrane with (c) 3 wt%, and (d) 7 wt%.

4. Conclusions

Nylon membranes have been successfully modified by plasma peroxide method together with grafting of PNIPAm via microwave-assisted irradiation. The grafted PNIPAm chains located mainly on the top surface and at the pore entrance of the membranes. The coverage of grafted PNIPAm chains on the membrane were inhomogeneously distributed but the uniformity was improved after the use of a pressure-assisted permeation technique. Addition of the crosslinker yielded a denser grafted membrane as compared to that of without one. The grafted membranes were fractured when grafting under the condition with the irradiation time over 15 min under 800 w because the solution temperature was higher than the operating temperature of membrane. The fractured membranes were unsuitable to be used for gating application because of unstable performances. Therefore, the PNIPAm-grafted membranes should be fabricated at a proper irradiation time of 10 min and under a proper output power of 800 w to obtain the maximum grafting yield. The critical concentration of NIPAm to give highest yield was found to be at 3 wt%. Membranes with different structures (linear chains or crosslinked networks) and different grafting yield are expected to affect their gating performance. The gating performance and thermo-responsive properties of the grafted membranes are under an ongoing investigation and going to be reported in the near future.

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Effects of Grafting Yield and Chain Structure on Oil-Water Separation of Poly(*N*-Isopropylacrylamide) Grafted Nylon Smart Membranes

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Abstract

The purpose of this study was to investigate oil-water separation performance of smart membrane by gravitational separation. The smart membrane, thermo-responsive membrane, was produced by grafting of poly(*N*-isopropylacrylamide) (PNIPAM) onto Nylon porous membrane using a nivel method prioerly reported. The grafting technique was a combined method of plasma peroxide technique and microwave-assisted polymerization. Two different grafted chain structures, linear and crosslinked network, were achieved by the absence/presence of a *N, N'*-methylenebisacrylamide (BIS) crosslinker. The membranes with different grafting yields were obtained by using different concentrations of *N*-isopropylacrylamide (NIPAM) solution in the grafting process. The membranes that were immersed in the solution containing NIPAM of 2-10 wt% were produced grafting yields of 7-47% and 9-135% for linear and crosslinked PNIPAM gates respectively. The oil–water separation ability of PNIPAM grafted membrane was found to be dependent on the grafting yield, the PNIPAM gate structure, and the environmental temperature. The membrane could separate oil-in-water and water-in-oil emulsions at temperatures below and above lower critical solution temperature (LCST) of PNIPAM, at 32°C, respectively. When the temperature lower than LCST, water selectively permeated through the membrane. Then, oil was retained above the membrane. Likewise, oil permeated easily through the membrane at the temperature higher than LCST. However, the permeation of oil was blocked when the membrane surface was covered by water. The crosslinked grafted membranes exhibited better separation efficiency than linear grafted membranes. It showed higher efficiency in separating oil-water emulsions with an increasing grafting yield, probably due to the decreased pore size of membrane. Furthermore, different oil–water emulsions could be separated by PNIPAM grafted Nylon membrane as well, an outstanding separation efficiency was also achieved.

Keywords: Porous nylon membrane; Poly(*N*-isopropylacrylamide); Thermo-responsive polymer; Thermo-responsive gating membrane; Gating performance; oil-water separation

BIOGRAPHY

Putita Katesripongsa was born on September 29, 1993 in Buriram, Thailand. She finished high school from Buriram Pittayakhom School in 2012. She attended Suranaree University of Technology (SUT) and graduated in 2016 with a Bachelor's degree in Chemical Engineering. She then continued her Master's degree in Materials Engineering at School of Polymer Engineering, Institute of Engineering, Suranaree University of Technology. During her graduate study, she got the Kittibandit scholarship from Suranaree University of Technology for financial support of her work. Her research was about PNIPAm grafted Nylon membrane by the novel synthesize technique. In the period of her study, she presented an oral presentation entitle: "An optimization of microwave-assisted grafting of poly(*N*-isopropylacrylamide) (PNIPAM) onto nylon-6 porous film for thermo-responsive gating membrane" at The 5th Asian Symposium on Material and Processing (ASMP) 2018 in Bangkok, Thailand and a poster presentation entitle : "Effects of grafting yield and chain structure on oil-water separation of poly(*N*-isopropylacrylamide) grafted Nylon smart membranes" at The International Conference on Materials Engineering and Nanotechnology ICMEN 2019 in Kuala Lumpur, Malaysia. Her work was published one paper entitled of "An optimization of microwave-assisted grafting of poly(*N*-isopropylacrylamide) (PNIPAM) onto Nylon-6 porous film for thermo-responsive gating membrane" in Mechanical Engineering Journal (2019).