



**Modification of Polysulfone Membrane for Separation of Compound
Substance in Natural Rubber Serum**

Soraya Ruangdit

**A Thesis Submitted in Fulfillment of the Requirements for the
Degree of Doctor of Philosophy in Physics (International Program)
Prince of Songkla University
2022**

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บทคัดย่อ

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ศึกษา และเมื่อนำเมมเบรนที่ผ่านการปรับปรุงด้วยเงื่อนไขดังกล่าวมาทดสอบการแยกซีรัมน้ำ
ขางพาราพบว่า ประสิทธิภาพของเมมเบรนดีขึ้นโดยให้อัตราการนำกลับของการซึมผ่านของรอบที่
สองมีค่าสูงถึง 95.9 เปอร์เซ็นต์ ค่าการกักกันปริมาณของแข็งทั้งหมดในซีรัมน้ำขางคือ 72.1
เปอร์เซ็นต์ และค่ากักกันโปรตีนทั้งหมดในซีรัมน้ำขางพารา คือ 91.5 เปอร์เซ็นต์ ซึ่งผลการทดลอง
ดังกล่าวแสดงให้เห็นว่า การปรับปรุงเมมเบรนให้มีความชอบน้ำโดยใช้ล้าอเล็กตรอนเพื่อการกราฟ
ติงสาร AAc/SSS สามารถปรับปรุงเมมเบรนให้มีความเหมาะสมต่อการแยกซีรัมน้ำขางพาราได้
อย่างมีประสิทธิภาพ

คำสำคัญ: รังสีอัลตราไวโอเลต, ล้าอเล็กตรอน, ความชอบน้ำ, เมมเบรนเทคโนโลยี, การแยกขางน้ำ
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Compound Separation in Natural Rubber Serum
Author Soraya Ruangdit
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ABSTRACT

Natural rubber product is the one significant exporting products of Thailand. Nevertheless, bad smells and wastewater from latex and rubber processing pollute the environment. Since the usable rubber particles in natural rubber latex are collected by chemical processing, the wastewater from the operation comprises the beneficial components in the residual fraction (NR serum). The NR serum consists of proteins, carbohydrates, fats, residual rubber particles, water, and other compounds. That compound will be transformed into products in the future, and value might be added to NR serum waste when it is separated from rubber particles and increased the concentration of the proteins and other components. Membrane technology is one popular technique that does not degrade organic molecules, and presents a more viable solution to the problem of separating NR serum from water. Nonetheless, membrane filtering of NR serum has been difficult due to tiny residual rubber particles in the serum, which are sticky and tend to clog the membrane, blocking pores and causing irreversible fouling. Improving the hydrophilic characteristics of the membrane surface is an essential factor in anti-fouling and preventing the accumulation of hydrophobic rubber molecules on the membrane surface. Thus, this research has the objective to enhance the hydrophilicity of the membrane surface by ultraviolet irradiation (UV-ray) with poly (ethylene glycol) (PEG) grafting, and by an electron beam to induce the acrylic acid/sodium styrene-sulfonate (AAc/SSS) grafting on the membrane surface. The results showed that the difference in wavelength of UV-ray had a different grafting effect. The UV-ray at a wavelength of 312 nm had better grafting and hydrophilic than 254 nm. Moreover, UV at treatment with 312 nm and the PEG grafting on the membrane showed a higher water flux than the untreated membrane. The electron beam energy at 10 MeV and dose of 50 kGy had shown the best condition for AAc/SSS grafting on the membrane surface. The modified membrane had been used for NR serum filtration, and the results showed after 2nd cycle filtrations of NR serum had the flux recovery ratios of 95.9 %, the rejection rates of the total solid content (TSC), and total protein in NR serum were 72.1 % and 91.5 %, respectively. So, the modified membrane had good anti-fouling properties toward the natural rubber particles and organic molecules found in NR serum.

Keywords: Ultraviolet irradiation, Electron-beam irradiation, Hydrophilicity, Membranes technology, Natural rubber filtration, Polysulfone membrane.

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LIST OF ABBREVIATION

AAc	Acrylic acid
AFM	Atomic force microscopy
BSA	Bovine serum albumin
CNF	Cellulose nanofibrils
DOG	Degree of grafting
DPPH	2,2-diphenyl 1-picryl hydrazide
DRC	Dry rubber component
e	Electron
FTIR	Fourier transform infrared spectroscopy
h	Hour
HCl	Hydrochloric acid
He	Helium
HEMA	2-hydroxy-ethyl methacrylate
kGy	Kilo Gray
LCN	Lignocellulose nanofibrils
LG	Surface tension between liquid and gas
MeV	Megaelectron-Volt
MW	Molecular weight
MWD	Molecular weight distribution
NaOH	Sodium hydroxide
nm	Nanometer
NMP	N-Methyl-2 pyrrolidone
NR	Natural rubber serum
PAN	Polyacrylonitrile
PEG	Poly (ethylene glycol)
PEO	Polyethylene oxide
pH	The positive potential of the hydrogen ions
PSF	Polysulfone
PTFE	Polytetrafluoroethylene
PVP	Polyvinylpyrrolidone
SE	Surface energy
SEM	Scanning electron microscopy
SG	Surface tension between solid and gas

LIST OF ABBREVIATION (CONTINUED)

SL	Surface tension between solid and liquid
SSS	Sodium styrene-sulfonate
TiO ₂	Titanium dioxide
TSC	Total solid content
UF	Ultrafiltration
μm	Micrometer
UV	Ultraviolet
WCA	Water contact angle
XPS	X-ray photoelectron spectroscopy
θ	Contact angle
% w/v	% weight/volume

LIST OF PAPERS

- Soraya Ruangdit, Suksawat Sirijarukul, Thawat Chittrakarn, Chaiporn Kaew-on. Enhancing hydrophilicity of polysulfone membrane surface by UV irradiation of different wavelengths and by PEG grafting, *Jurnal Teknologi*, 83:4 (2021) 111–117. doi.org/10.11113/jurnalteknologi.v83.1638.
- Soraya Ruangdit, Thawat Chittrakarn, Chaiporn Kaew-on, Ritiron Samran, Weerapong Bootluck and Suksawat Sirijarukul. E-beam induced grafting of binary monomer on polysulfone membrane for the separation of skim natural rubber latex, *Journal of Environmental Chemical Engineering*, (2022) S2213-3437(22)00735-7. doi.org/10.1016/j.jece.2022.107862.

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PAPER-II

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**E-beam Induced Grafting of Binary Monomer on Polysulfone Membrane for the Separation of Skim Natural Rubber Latex**

Author: Soraya Ruangdit, Thawat Chittrakarn, Chaiporn Kaew-on, Ritiron Samran, Weerapong Bootluck, Suksawat Sirijarakul

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CHAPTER 1

INTRODUCTION

1. Introduction

Natural rubber product is the one significant exporting products of Thailand. Thailand's rubber industries had concentrated latex factories, smoked rubber factories, and processing sectors including tires and rubber gloves, and others. The rubber industry generates revenue for the country's citizens, yet also harms the environment. Because the fresh rubber latex comprises approximately 25-45% dry rubber component (DRC) was processed, and others were a waste [1]. The rubber waste is composed of small rubber molecules, protein, sugar, and others, released from the factory that cause odors, wastewater, and pollution due to the degradation of protein, and others. The unusable components in the remaining fraction (NR serum) consist of small rubber particles, carbohydrates, proteins, Lutoid, Frey-Wyssling particles, and others [2]. Such components in the serum should not be left without benefits. Devaraj et al. deployed membrane technology to reduce waste and recover value-added goods from waste in a rubber manufacturing facility for water recycling [3]. So, the membrane process is an attractive alternative technique for separating the substances from serum. However, membrane filtration of NR the serum has challenges owing to the combination of tiny residual rubber particles in the serum, which are sticky and tend to clog the membrane, blocking pores and causing irreversible fouling [4], [5]. Furthermore, improving the hydrophilic characteristics of the membrane surface is one technique to reduce the accumulation of hydrophobic rubber molecules.

Polysulfone (PSF) is a high-potential and widely used polymer for membrane development because of its advantages, including excellent chemical, mechanical, and thermal resistance [6]. On the other hand, the PSF membrane has a hydrophobic characteristic that reduces water flux and increases fouling which is a disadvantage. Many studies have increased the hydrophilic property of the membrane surface by modifying the PSF membrane surface. Physical technologies such as ultraviolet irradiation (UV) and plasma treatment are also commonly used to improve membrane surfaces. The UV irradiation with hydrophilic polymer grafting is inexpensive, basic,

and well effective [7], [8]. The common additive in membrane composition is Poly (ethylene glycol) (PEG). It has low toxicity and is inexpensive, as well as the ability to dissolve in water and organic solvents. PEG has been shown to have useful properties such as increased hydrophilicity and permeability [9]. Nevertheless, the PEG has low mechanical and thermal properties making it difficult to graft onto the PSF membrane surface [10]. Thus, the PEG grafting on the PSF membrane by the different UV wavelengths was studied in this work.

Another highly efficient alternative for the PSF membrane improvement is electron beam (e – beam) irradiation. Xi et al. [11] examined the influence of monomer concentration and e-beam irradiation dose on the formation of hydrophilic groups on a membrane surface. The hydrophilicity of the membrane was improved by grafting a binary monomer of sodium styrene-sulfonate and acrylic acid (AAc/SSS). The surface grafting of sodium styrene-sulfonate (SSS) is an exciting method due to the SO_3^- group is a strong hydrophilic group [12]. However, SSS has been successfully grafted onto various polymeric membranes with the aid of acrylic acid (AAc) [13]. Therefore, this research focuses on using the e-beam energy to assist AAc/SSS grafting, then investigates the antifouling property of the modified membrane during NR serum filtration.

2. Objectives

The research project aims to modify the PSF membrane surface for separation the components of natural rubber serum (NR serum), natural rubber latex and enhance the following properties:

1. To prepare ultrafiltration polysulfone membrane.
2. To improve PSF membrane surface by UV-assisted grafting of Poly (ethylene glycol) (PEG)).
3. To improve hydrophilic properties of PSF membrane surface by using the electron beam technique with AAc/SSS.
4. To apply the modified membrane for separation of a compound substance from the NR serum.

CHAPTER 2

BACKGROUND

1. Natural Rubber Latex

1.1 Components of natural rubber latex

Natural rubber (NR) is a colloidal suspension of rubber particles in an aqueous phase obtained from a rubber plant, acquired by cutting from *Heavea brasiliensis* rubber plants. Depending on the type of the planting material, fresh field latex has around 25-45 % dry rubber content (DRC) and 5-10% non-rubber components. Proteins, carbohydrates, lipids, and inorganic salts are among the non-rubber components, shown in **Table 1** [1], [13].

Table 1 Composition of fresh natural rubber latex [14].

Composition	Latex		Dry rubber
	Fresh latex (% w/v)	Dry matter of latex (% w/v)	Dry matter (% w/w)
Rubber hydrocarbon	35.0	87.0	94.0
Protein	1.5	3.7	2.2
Carbohydrate	1.5	3.7	0.4
Lipids	1.3	3.2	3.4
Organic solutes	0.5	1.1	0.1
Inorganic substances	0.5	1.2	0.2

Natural rubber is a hydrocarbon with a high molecular weight. Rubber's molecular structure is comprised of C_5H_8 isoprene units connected at the C1 and C4 carbon atoms as shown in Figure 1 [15].

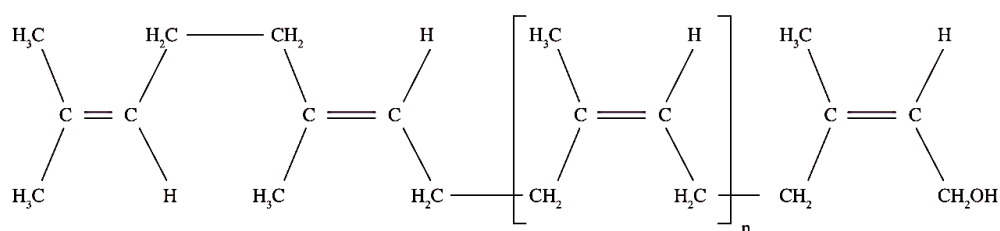


Figure 1 Chemical structure of cis-1, 4-polyisoprene from natural rubber [16].

The size of rubber particles in fresh latex varies according to the age of the rubber trees. Large and micro rubber particles were discovered in the natural rubber latex of mature plants. The average size of rubber particles is shown in Figure 2, with concentrated latex and skim latex having sizes around 3-0.1 μm and 0.3-0.05 μm ,

respectively [17]. *Hevea brasiliensis* natural rubber is a polymer with a very high molecular weight (MW) and a wide molecular weight distribution (MWD).

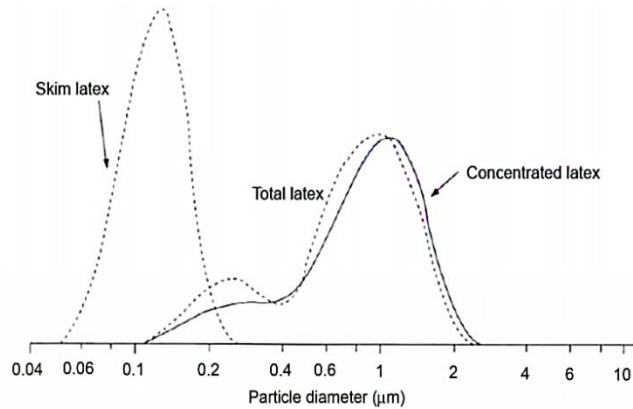


Figure 2 Particle size distribution of fresh field latex [18].

1.2 Rubber matters composition

Fresh latex can be separated into four main fractions by centrifugation: a top layer of rubber, an orange or yellow layer containing Frey-Wyssling particles, a colorless serum phase, and a bottom fraction containing luteoid particles, shown in Figure 3.

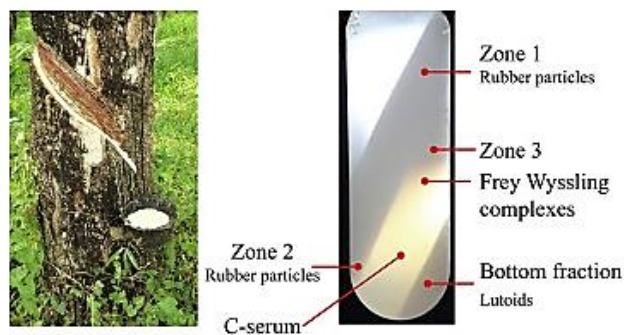


Figure 3 The fraction after centrifugation of natural rubber latex [19].

Rubber particles in natural rubber latex are spherical hydrocarbon droplets that are stabilized by the negative charge of surface absorbed proteins and lipids, shown in **Figure 4**. [20].

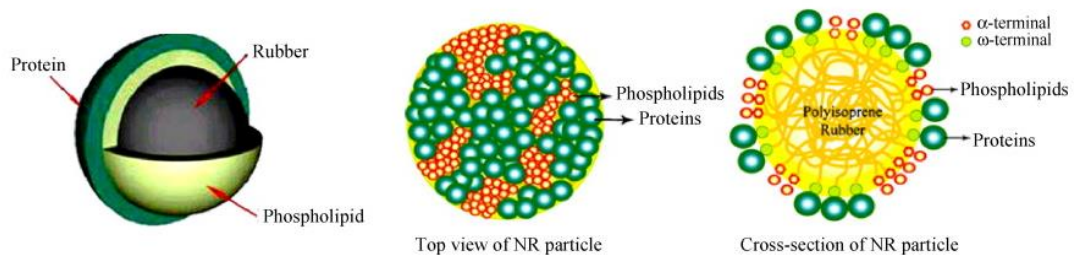


Figure 4 The structure models of the rubber latex particle surface [21].

Lipids are water-insoluble components found mostly in the rubber phase, with modest amounts in the bottom fraction and Frey – Wyssling particles, neutral and polar lipids are the two types of lipids that exist. The most important neutral lipid in natural rubber is tocotrienol, which is a vitamin E derivative [22]. About 25% of all proteins in latex are found on the outer layer of rubber particles. Alpha-globulin is almost of the proteins found in the outer layer of rubber particles and Hevien alpha-globulin is the remaining protein [2].

1.3 Non Rubber matters composition

Non-rubber solutions are mainly composed of water and serum, which are comprised of carbohydrates, proteins, amino acids, and other substances. Approximately 1% carbohydrate content is sugar and starch. The other components as Quebrachitol, glucose, fructose, sucrose and the protein content of alpha-globulin are in the serum fraction [23].

The lutoid particle is vacuoles in latex next to rubber particles. Inside of lutoid particle consists of aqueous containing components such as acids, mineral salts, proteins, sugar, and polyphenol oxidase [23].

The Frey-Wyssling particle is bigger than the rubber particles. However, it has a lower density than rubber particles. Lipid and carotenoid particles comprise the Frey-Wyssling particles. The Non-rubber constituent in latex is shown in **Table 2**.

Table 2 Non-rubber constituent in latex [24].

Constituents	Percentage by weight of the latex
Fatty acid soap (e.g. ammonium oleate)	0.5
Sterols and sterol esters	0.5
Proteins	0.8
Quebrachitol	0.3
Choline	0.1
Glycerophosphate	0.1
Water-soluble carboxylic acid salts (acetate, citrate, etc.)	0.3
Amino acid and polypeptide	0.2
Inorganic salts (ammonium and potassium carbonate and phosphate, etc.)	0.2

2. Membrane

The membrane is a selective barrier that permits some selective matters to penetrate but blocks some others. The membrane is made from organic or inorganic material. Membranes made from inorganic materials have higher separation properties than that organic materials, but it is more expensive than organic material [25]. Nowadays, there is an interest in developing membranes from organic materials such as polymers to have a higher separation property [26]. Polymer membrane is a popular material because it can be modified and can be made in various forms, such as hollow fiber and flat sheets. The membrane structure can be classified into 2 types, asymmetric and symmetric structure. There are many types of symmetric membrane classified by using porosity properties such as microfiltration, ultrafiltration, nanofiltration, and reverse osmosis [27] as shown in **Figure 5**.

Cut-offs of different liquid filtration techniques	
	0,001 0,01 0,1 1 10 100 1000
Micrometer logarithmic scaled	
Angstroms logarithmic scaled	1 10 100 1000 10 ⁴ 10 ⁵ 10 ⁶ 10 ⁷
Molecular weight (Dextran in kD)	0,5 50 7.000
Size ratio of substances to be separated	<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">Solved salts</div> <div style="text-align: center;">Pyrogens</div> <div style="text-align: center;">Viruses</div> <div style="text-align: center;">Bacteria</div> <div style="text-align: center;">Yeast</div> <div style="text-align: center;">Pollen</div> <div style="text-align: center;">Sand</div> </div> <div style="display: flex; justify-content: space-around; align-items: center; margin-top: 5px;"> <div style="text-align: center;">Atomic radius</div> <div style="text-align: center;">Sugar</div> <div style="text-align: center;">Albumin (66 kD)</div> <div style="text-align: center;">Red blood cells</div> <div style="text-align: center;">Human hair</div> </div>
Separating process	<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">Reverse osmosis</div> <div style="text-align: center;">Ultra filtration</div> <div style="text-align: center;">Particle filtration</div> </div> <div style="display: flex; justify-content: space-around; align-items: center; margin-top: 5px;"> <div style="text-align: center;">Nano filtration</div> <div style="text-align: center;">Micro filtration</div> </div>

Figure 5 Cut-offs of different liquid filtration techniques.

The filtration process can be classified based on the flow direction of suspended materials. The two types of filtration processes are dead-end and cross-flow filtration, as shown in Figure 6.

In dead-end filtration, the solution is forced perpendicularly over the membrane by external pressure. This approach has the advantage of allowing the solution to move quickly through the membrane. On the other hand, the ease with which fouling and cake layers build on the surface membrane is a disadvantage of this approach.

In cross-flow filtration, the solution is fed parallel through the membrane. This filtration technique is well suited for the use of a highly concentrated solution because it reduces membrane fouling and pore blockage [28].

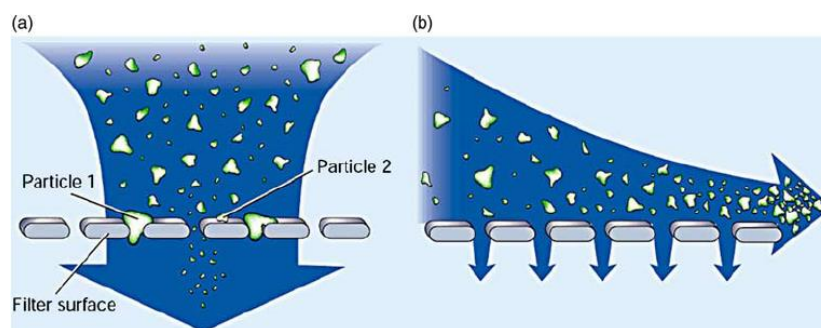


Figure 6 Membrane process. (a) Dead-end filtration, (b) Cross -flow filtration [28].

The diffusion of a solvent through a permeable membrane from a dilute solution to a concentrated solution by the driving force of chemical potential is known as osmosis [29].

Polysulfone (PSF) polymer has excellent mechanical, biological, and chemical stability, a wide operating range at temperature, and pH value [30]. PSF is one of the most important polymeric materials used in the biomedical. The chemical structure of PSF is shown in **Figure 7**. PSF membranes are used as hemodialysis hollow fiber with high permeability for low-molecular-weight proteins [31]. Moreover, the PSF polymer is popular for membrane technique, but it has hydrophobic properties. The hydrophobic membrane cause membrane fouling. So, a lot of research has been done to improve the membrane to be hydrophilic property, for anti-fouling [32]–[34].

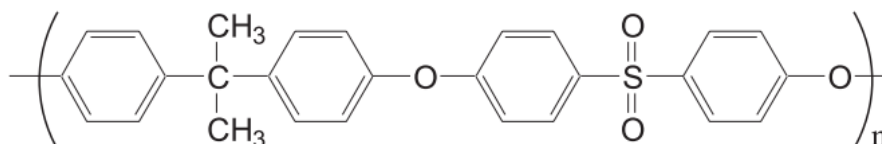


Figure 7 Chemical structure of polysulfone (PSF) [35].

3. Membrane modification

3.1 Hydrophilic property

The polymer used in the production of membranes is mostly hydrophobic polymers because most structures are composed of C-H. Improving the membrane for hydrophilicity has attracted many research groups. Ding et al. modified the membrane by a coating of Lignocellulose nanofibrils (LCN) and cellulose nanofibrils (CNF) on the surface of polysulfone membranes; the result showed an increase in hydrophilic and pure water flux [36].

Contact angle (θ) is the angle at which the liquid-gas interface meets the solid-liquid interface. The contact angle is determined by the resultant between adhesive and cohesive forces. So, the contact angle provides an inverse measurement of hydrophilicity. The contact angle between a solid and a liquid depends on the surface tension between solid and gas (SG), the surface tension between solid and liquid (SL), and the surface tension between liquid and gas (LG), as shown in **Figure 8**. A contact angle (θ_c) less than 90° and greater than 90° indicates that wetting of the surface is hydrophilic and hydrophobic, respectively [37], [38].

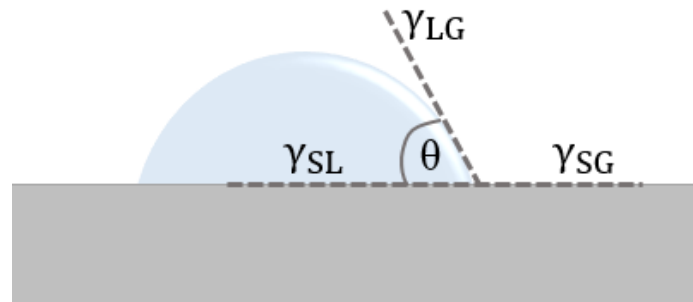


Figure 8 Contact angle between a solid and a liquid.

The contact angle is used to calculate the surface energy of the membrane surface. The polar and dispersive components are responsible for the hydrophilic and hydrophobic properties. The surface energy can be calculated by equation (2)

$$\gamma_{LV}(1 + \cos\theta) = 2(\gamma_L^d \cdot \gamma_S^d)^{1/2} + 2(\gamma_L^p \cdot \gamma_S^p)^{1/2} \quad (2)$$

The liquids that will be used for calculating surface energies of membranes are water Formamide and Ethylene glycol with known γ^p (polar component) and γ^d (dispersive component) [39], [40].

Many significant polymer applications necessitate good adhesion to other molecules. Adhesion is a manifestation of the attractive forces that exist between all atoms and which fall into broad categories: primary quasi-chemical (hydrogen bond) and secondary (van der Waals) [39]. That can be estimated as the polar components and dispersive components in equation (2)[38]. The surface energy of the membrane surface

is the significant result of decreasing the water contact angle and then attracting the water molecule passing the membrane and increasing the flux.

3.2 The PEG grafting by UV-ray

Polyethylene glycol (PEG) is a versatile polyether utilized in various applications, particularly in medicine. Polyethylene oxide (PEO) is another name for PEG, the formulation is shown in **Figure 9** [41]. The PEG is the most common additive used in membrane formulation. It can be dissolved in water and organic solvent, with low toxicity, and cost. PEG has shown promising potential in increased hydrophilicity [39]. Chittrakarn et al. [42] studied the PSF surface grafting by PEG grafting with Ar/O₂ plasma. The modified membrane was permanent hydrophilic properties.

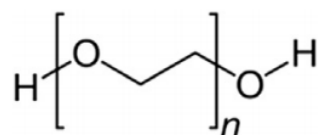


Figure 9 Chemical structure of polyethylene glycol [41].

UV irradiation technique is widespread use to improve the membrane surface properties because it can work at atmospheric pressure and can change membrane surface properties without adverse influence on the bulk properties [41].

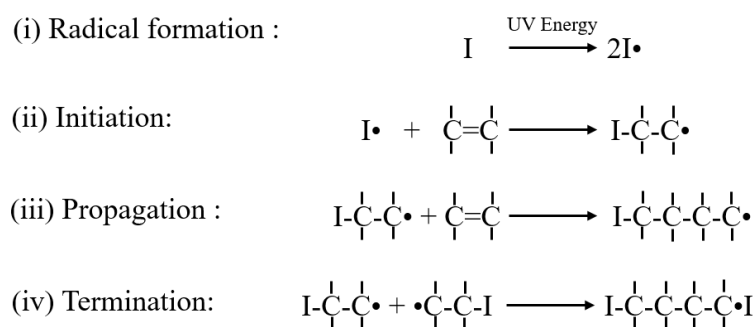


Figure 10 UV-free radical polymerization process [43]

UV can generate free radicals on the membrane surfaces by cutting chemical bonds of atoms or molecules. UV-ray interaction with polymers, the polymer absorbs light energy and creates a radical species. In the initiation step, the radical species will react with the bonds of the polymer such as C-H, C-C, and others. In the propagation step, the reactive species will respond with others to form a new radical where the polymerization process has occurred. This process will be terminated when two growing polymer chains react with each other, as **Figure 10** [43], [44]. However, the reaction depends on the polymer's structure and UV energy due to the difference in bond dissociation energies in diatomic molecules such as C-H (338.4 kJ mol⁻¹), C-C

(618.3 kJ mol⁻¹), C-O (1,076.38 kJ mol⁻¹) [45], [46]. The UV wavelength energy was calculated using Planck's equation (3) [47], [48]. UV wavelength, UV treatment time, and polymer type all influence the activity of UV energy on polymer surfaces [49], [50].

$$E = h\nu = \frac{hc}{\lambda} \quad (3)$$

Chemical changes by UV exposure result in bond dissociation, the result is chain scission and/or crosslinking; subsequent reactions with oxygen result in the formation of functional groups such as carboxyl (COOH), or carbonyl (C=O) [51], [52]. The UV affects photo-degradation, which usually affects only the top few micrometers of the surface (50 - 100 μm) [53]. The effect of UV is dependent on the action of temperature, moisture, exposures time, wavelength, and others [51]. Bormashenko et al., [54] reported that when polymers are exposed to electromagnetic radiation, experience chemical, and physical modification. It was revealed that PSF was subjected to UV irradiation in an atmosphere of oxygen release, the short-chain of the polymer contained most of the oxygen absorbed by the polymer which significantly decreased the contact angle. Moreover, the result had shown decreasing in water contact angle when increasing the UV treatment time. Konruang et al. [7] investigated the effects of UV for surface modification of asymmetric PSF membranes. The PSF membranes were prepared by the phase inversion method. The surface of membranes was modified by UV with 254 and 312 nm wavelengths. The results were shown that the PSF membranes were hydrophilicity on the surface after the UV treatment indicated by the reduction of water contact angle with increasing treatment time. The different wavelengths were shown in the different water contact angles (WCA). The UV at 312 nm had a lower WCA than the UV at 254 nm, which represents higher hydrophilicity. Homayoonfal et al. [55] studied the polysulfone membranes that were prepared by phase inversion and modified by UV-induced polymerization of AAc and PEG of different molecular weights. The results show that by increasing irradiation time and monomer concentration in the photo-grafting process, pure water flux declines, and salt rejection increases. Because of the pore size and high surface charge density, the developed membranes show a promising capability for water desalination.

A PSF membrane surface irradiated with UV and PEG grafting was found to have enhanced hydrophilicity and water flux [56]. PEG has been used in numerous studies to reduce the problem of free radical disintegration on membrane surfaces, which causes reversal back to hydrophobicity because it is hydrophilic with long chains. Due to its poor mechanical and thermal properties, grafting PEG on membrane surfaces is challenging. As a result, PEG grafting using UV has been considered as a possible proper solution. PSF membrane surfaces exposed to high-energy UV radiation may suffer to find a balance between crosslinking and chain scission [57]. As a result, the

duration of the treatment and the wavelength of the UV light was critical in improving the membrane surface.

3.3 The SSS/AAc grafting by electron beam

Sodium styrene-sulfonate (SSS) has been used in many fields, including biomedical and electrical applications [58]. The sulfonate group (SO_3^-) in SSS, shown in **Figure 11(A)**, a hydrophilic monomer has good anti-fouling properties, because of its high electrostatic force and hydration sphere around the sulfonate group [8], [59]. However, the SSS is hardly grafted on the PSF membrane because their hydration spheres are disagreeable with a hydrophobic PSF membrane and cannot diffuse into the membrane bulk, and the incompatibility of the highly ionized and hydrophilic sulfonate group with hydrophobic polymers [60]. However, the SSS has been successfully grafted onto PSF membranes by acrylic acid (AAc) [13], [61]. The AAc grafted into a polymer membrane has previously improved the compatibility of the membrane with SSS [59], due to the AAc having both hydrophilic and hydrophobic sites on the structure, shown in **Figure 11(B)**. So, AAc and SSS will be used as hydrophilic substances to modify the PSF membrane surface. Moreover, many researchers used the irradiation method to induce AAc/SSS grafting on the membrane surfaces, presenting a good grafting yield [12], [59].

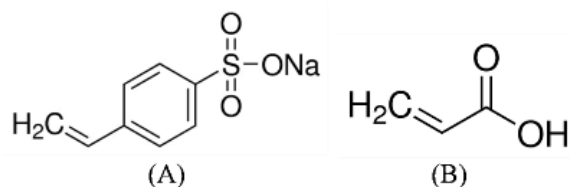


Figure 11 Chemical structure of acrylic acid (AAc) [62] and sodium styrene-sulfonate (SSS) [63].

The use of physical techniques such as UV irradiation and plasma treatment to enhance membrane surfaces is popular. UV irradiation is low-cost, but it takes a long time to set up [8]. Low-pressure plasma treatment is highly efficient, but the low-pressure setup required limits the area of the membrane and takes a long time to develop the required pressure [64]. Irradiation with an electron beam (e^- beam) is a highly efficient technique. Despite traditional low-pressure plasma treatment, this method does not necessitate the use of expensive vacuum equipment. Large-scale industrial applications are available due to the process's simplicity and low cost [11]. The electron-induced mechanism can be stated in the following method. When ionizing radiation activates polymer molecules, the electrons cause chain scissions and hydrogen abstractions in the polymer chains, resulting in the formation of free radicals. Cleavage of carbon-hydrogen bonds produces radicals that are extremely unstable and quickly

disappear, resulting in cross-linking or recombination with other monomers, whereas cleavage of main chain carbon-carbon bonds produces chain-end radicals [65], [66].

The electron beam irradiation has many advantages for modification of membrane. The radiation-induced process is temperature independent. It is free from contamination as no catalyst or additives are required. The electron beam can produce a free radical in the bulk membrane while penetrating the polymer membranes. And this method produces fewer homopolymers since the monomers are not directly exposed to radiation. The electron beam irradiation treatment requires no expensive vacuum equipment, on the other hand, the plasma treatment must use the vacuum system for making a low-pressure plasma. So, the electron beam technology is a simple and low-cost treatment [11], [67].

The electron beam interactions have been a discrepancy in regard to the interpretation of the mechanisms of chain-scission and cross-linking for electron irradiated. The energy deposited per unit ion path length is measured in linear energy transfer (LET), which is frequently given in SI units of eV/nm/ion or eV/nm. When a high-energy particle reaches a polymer medium, it releases energy in two ways: by interacting with atomic nuclei and by interacting with target electrons. The former is referred to as nuclear stopping, whereas the latter is referred to as electronic stopping. Collisions between the energetic particle and the target nuclei cause nuclear energy loss, which is nuclear energy loss due to inelastic collisions (nuclear reactions). The momentum transfer from electron or ion to target atom and the interatomic potential between two atoms are used to quantify nuclear stopping. Electronic stopping has been mostly determined by the ion's charge state and velocity. When an electron passes through a material, its valence electrons are stripped away in variable levels depending on the electron or ion velocity (V_{ion}) and Bohr (orbital electron) velocity (V_B), as equation (4). Where, Z is atomic number, a and b are fitting constants. Moreover, a maximum in the electronic stopping occurs around the Bohr velocity, which is LET given by equation (5) when N is the atomic density of target [68], [69].

$$Z_{eff}^* = Z \left[1 - a \exp \left(-b \frac{V_{ion}}{V_B} Z^{-2/3} \right) \right] \quad (4)$$

$$NS(E) = \frac{dE}{dx} \quad (5)$$

From the equation, the interaction depends on the type of target or polymer type due to different atomic numbers, atomic density, and electrons beam energy. Thus, the modification of the PSF membrane was the different conditions of the electron energy, electron dose, and the polymer membrane.

CHAPTER 3

PAPER I

Polysulfone (PSF) is one of the popular polymer membranes due to its good chemical and mechanical properties. However, the PSF has natural hydrophobicity and is easy to have severe fouling. Poly(ethylene glycol) (PEG) grafting on the PSF membrane is one technique to improve the property of the membrane and decrease fouling because the PEG is natural hydrophilicity. Nevertheless, PEG has low thermal properties and poor mechanical results in difficulty grafting PEG on the PSF membrane surface. Physical treatment with gamma, plasma, and ultraviolet radiation (UV) has high efficiency for inducing the grafting process to polymer membrane. The UV is a basic technique, low cost, and doesn't require a low-pressure system in processing. Furthermore, UV has a broad wavelength range, with each wavelength having unique energy and different effect on the membrane surface. So, this study aims to investigate the effect of the 312 nm and 254 nm wavelengths of UV on the PEG grafting of the PSF membrane. The wettability of the modified membrane surfaces was investigated by interpreting the results of surface morphology, water contact angle (WCA), surface energy (SE), functional groups, water flux, and salt rejection. The results indicated that when exposed to UV light for up to 72 hours, the 312 nm wavelength produced lower WCA than the 254 nm wavelength. The treated PSF membrane was effectively enhanced and retained increased hydrophilicity for up to thirty days after being irradiated at 312 nm for 72 hours and then PEG grafted.

PAPER I

Enhance hydrophilicity of polysulfone membrane surface by UV irradiation of different wavelengths and by PEG grafting.

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ENHANCING HYDROPHILICITY OF POLYSULFONE MEMBRANE SURFACE BY UV IRRADIATION OF DIFFERENT WAVELENGTHS AND BY PEG GRAFTING

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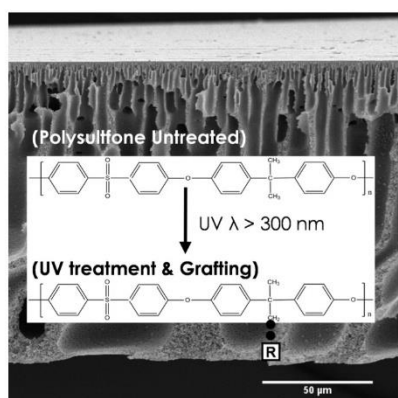
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Graphical abstract



Abstract

Polysulfone polymer (PSF) membrane has disadvantages due to its hydrophobicity, which may cause fouling and reduce separation performance. Therefore, this study aimed to enhance the hydrophilicity of PSF membranes by using irradiation at different ultraviolet (UV) wavelengths, followed by Poly(ethylene glycol) (PEG) grafting on the PSF surfaces. The hydrophilicity of the treated membrane surfaces was examined by measuring water contact angle (WCA), surface energy (SE), surface morphology, functional groups, salt rejection, and water flux in a filtration instrument. The results show that with long UV treatment for up to 72 h, the 312 nm wavelength gave lesser WCA than treatment at 254 nm. The treated PSF membrane irradiated at 312 nm for 72 h, followed by PEG grafting, was effectively improved and retained increased hydrophilicity for up to thirty days.

Keywords: UV treatment, PEG-grafting, Surface modification, hydrophilicity, polar component

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1.0 INTRODUCTION

Membrane technology is pervasive in the industry. Polysulfone (PSF) has been widely used as a polymer in the commercial production of microfiltration and ultrafiltration membranes, due to several advantages, such as good mechanical, chemical, and thermal properties, and easy film-forming [1, 2]. However, PSF membranes tend to have severe fouling during filtration due to natural hydrophobicity, low surface energy, and non-ionic character [3]. The membrane surface properties play a key role in the interactions

with atoms or molecules or other active particles. Many polymers that have been used in membranes are hydrophobic with a low surface energy, such as poly(ethylene terephthalate) (24.2 mN/m), poly(propylene) (29.5 mN/m), and poly(vinylidene fluoride) (42-47 mN/m) [4,5]. If the membrane surface is hydrophilic with a high surface energy, this reduces fouling due to electrostatic repulsion of other molecules from the membrane surface [6]. Several methods have been used in many studies to improve membrane surface energy, such as coating with a hydrophilic polymer for increased hydrophilicity of

the PSF membrane [7], or by blending in hydrophilic or organic materials or some minerals [8, 9]. Physical treatment with plasma is a popular technique due to its high efficiency. However, the weakness of this technique is that it still requires a low-pressure system for processing [10, 11]. Ultraviolet (UV) irradiation is another technique that is in widespread use to improve the surface properties, because it can work at atmospheric pressure and can change membrane surface properties without adverse influence on the bulk properties [12]. UV light can generate free radicals on the membrane surfaces by cutting chemical bonds of atoms or molecules. A PSF membrane surface irradiated with UV followed by Poly(ethylene glycol)(PEG) grafting was found to have enhanced charge density and pure water flux [13]. Many studies have used PEG as a membrane component to solve the problem of free radical disintegration on the membrane surfaces, which causes reversal back to hydrophobicity, because PEG is hydrophilic with flexible chains. However, it is difficult to put PEG on the membrane surfaces due to its poor mechanical and thermal properties. So, PEG grafting with UV light assistance has been studied to address these problems. The high-energy UV irradiated PSF membrane surfaces can struggle for balance between crosslinking and chain scission, causing a decreased water flux [14]. The membrane grafted with UV assistance was found to have improved antifouling performance [15]. The mechanism of polymer membrane improvement can be described as follows. In the first step, high-energy UV light generates free radical polymers. After that, the radical species will interact with other functional materials in the second step. The further interactions in the second step and the interactions between particles in the second step along with other functional materials continues until saturation [16].

The natural UV-rays have a wide wavelengths range (200-400 nm) and each wavelength has a different quantum energy [17]. So, irradiation by different UV wavelengths for different treatment times can provide different surface properties. Such factors may affect PEG grafting on the membrane surface with UV assistance. So, this investigation studied the effects of different UV-ray wavelengths and treatment times for improving hydrophilicity properties of PSF membranes by grafting with PEG, and studied the permanence or longevity of the hydrophilicity improvement.

2.0 METHODOLOGY

Polysulfone (PSF) Udel P-1700 as pellets was supplied by Solvay (China). Polyvinylpyrrolidone (PVP, K30) and Poly (ethylene glycol) (Mw 8,000) (PEG) were purchased from Sigma-Aldrich, while N-Methyl-2-Pyrrolidone (NMP) was supplied by ACI Lab-scan (Thailand). Sodium chloride (NaCl) was purchased from Ajax Finechem.

The dope solution for this work was prepared by mixing 17.5 wt% PSF, 0.5 wt% PVP and 82 wt% NMP. The PSF pellets were dried at 80 °C for 24 h in a vacuum oven (BINDER, VD53) before use. To prepare the dope solution, PVP and NMP were mixed in a beaker before stirred for 10 min with a magnetic stirrer. Then, PSF pellets were added into the solution under vigorous stirring for 24 h. After that, the solution was ultra-sonicated in an ultrasonic cleaner (GT SONIC, VGT-1620T) for 30 min to remove any bubbles. Subsequently, the free bubble dope solution was cast on a smooth clear glass plate followed by instantaneous immersion in reverse osmosis (RO) water coagulation bath at room temperature (23 °C) for wet phase inversion, to form a wet thin membrane. After peeling off from the glass plate, the membrane was placed in a second RO water bath and was soaked for 24 h to remove the solvent. Afterwards, the membrane was desiccated in ambient conditions for 24 h and dried in a vacuum oven at 70°C for 24 h before use.

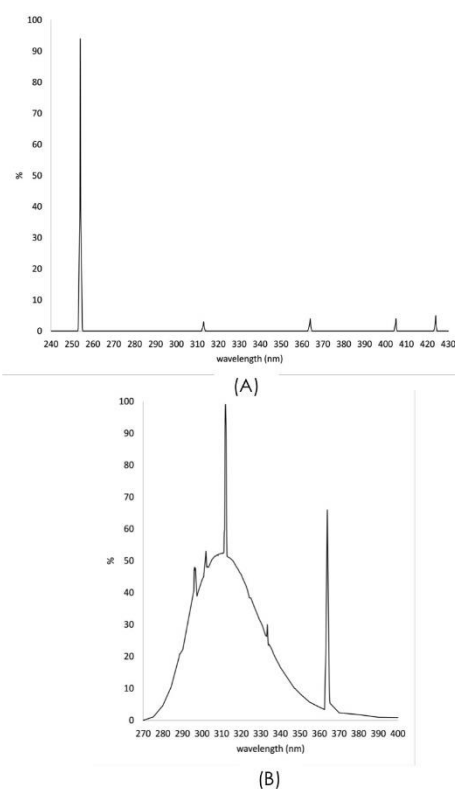


Figure 1 The spectra of UV sources for (A) 254 nm, and (B) 312 nm nominal wavelengths

The optimized membrane surface was irradiated by UV radiation in the ambient atmosphere ($25 \pm 2^\circ\text{C}$ and 60-65% relative humidity, measured by Traceable Digital Thermohygrometer, Cole-Palmer (Thailand)). The sample membranes were exposed to UV source (15W-254 nm or 15W-312 nm, Vilber Lourmal, VI-215. MC (France)) for different conditions shown in Table 1 while the distance between the membrane sample and the UV source was kept fixed at 20 cm. The spectrum of UV source for this experiment was characterized by using a laser power meter, Coherent Inc.; GES-UM2, shown in Figure 1A and 1B [18]. After the UV treatment, the membrane was immersed in PEG solution (1.0 wt%) for 3 h. After that, the treated membrane was soaked in RO water for 24 h before drying in ambient air at room temperature for 12 h before testing. After treatment process was complete, the first set of the treated membrane was verified by measuring WCA and the other set of dry membranes was retained in ambient air at temperature of 23-25 °C and relative humidity of 66 – 68 % for 30 days before testing

Table 1 The conditions of UV treatment membrane

Condition		5 h	10 h	24 h	48 h	72 h
UV 254 nm	No PEG	A5	A10	A24	A48	A72
	PEG	B5	B10	B24	B48	B72
UV 312 nm	No PEG	C5	C10	C24	C48	C72
	PEG	D5	D10	D24	D48	D72

The morphology of the treated membrane was investigated on top side, bottom side and in a cross-section by using a Scanning Electron Microscope (SEM, JSM-5800 LV). The hydrophilicity of the treated membrane was examined by measuring the water contact angle (WCA) and the surface energy (SE). The measurement of contact angle was done with three types of liquid: water, Formamide and Ethylene glycol with known γ^p (polar component) and γ^d (dispersive component). The SE was calculated with Equation (1) [19, 20].

$$\gamma_{LV}(1 + \cos\theta) = 2(\gamma_L^d \cdot \gamma_S^d)^{1/2} + 2(\gamma_L^p \cdot \gamma_S^p)^{1/2} \quad (1)$$

The functional groups on the PSF membrane surface were assessed by using attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy (Bruker, Hyperion 3000).

Before membrane testing, the membrane was immersed in water for 1 hour. After that, the reverse osmosis water was forced through each treated membrane in a cross-flow process at 0.1 MPa to characterize the water flux ($\text{L m}^{-2} \text{h}^{-1}$) using Equation (2) [9, 21].

$$\text{Flux} = \frac{V}{A \times t} \quad (2)$$

Here V is the volume of the filtrate (L or dm^3), A is the practicable area of the membrane (m^2) and t is the testing time (h).

The rejection rate was also used to assess the treated membrane properties after 30 min of filtration. The conductivities of permeate and feed solution were measured by using Eutech Instruments, Syberscan PC300 (Singapore). The rejection ratio (R) was calculated according to Equation (3).

$$R(\%) = 1 - \frac{C_p}{C_f} \times 100\% \quad (3)$$

Here C_i and C_p are the Sodium chloride (NaCl) concentrations of permeate and feed solution (1 molar), respectively.

3.0 RESULTS AND DISCUSSION

The hydrophilicity properties of the variously treated PSF membranes were examined by measuring WCA and SE, with results shown in Figure 2. For the treatment times from 0 to 10 h, WCA after treatment at UV wavelength 254 nm (UV254) was lower than after treatment at 312 nm (UV312), as shown in Figure 2(A). This means that for treatment times shorter than 10 h, the hydrophilicity with UV254 was better than with UV312. However, for treatment times exceeding 10 h, the WCA with UV312 was less than that with UV254; for comparatively long treatments up to 72 h, the hydrophilicity with UV312 was better than with UV254, as shown in Figure 2(A).

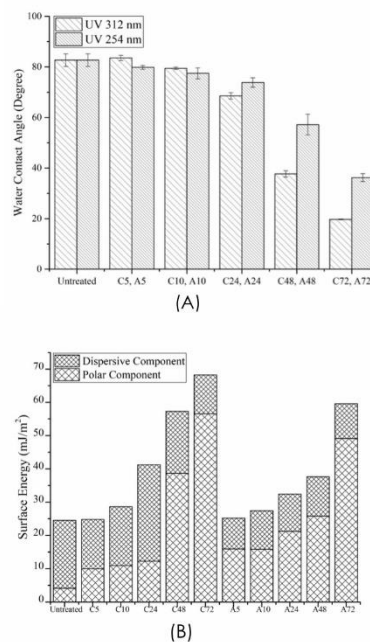


Figure 2 The water contact angles (A), and surface energies (B) of membranes treated with UV254 and UV312 for various treatment times (without PEG grafting)

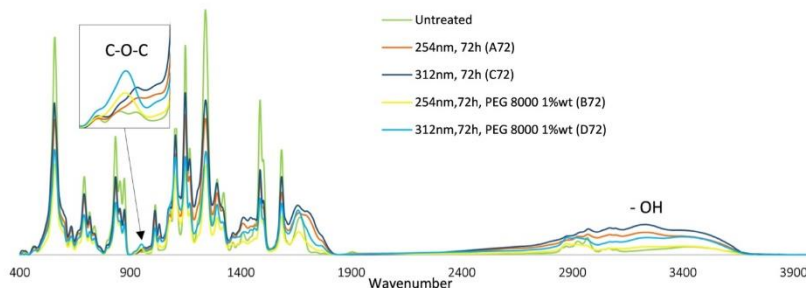


Figure 3 The FTIR spectra of membranes treated for 72 h with UV254 or UV312, with or without grafted

Furthermore, the membrane surface energies matched the WCA results. After UV treatment for 72 h, the SE with UV254 and UV312 treatments had increased from 27.7 mJ/m² for untreated membrane to 68.2 and 59.9 mJ/m², respectively. In addition, the surface energy consists of a dispersive component that represents non-polar forces between non-polar molecules and of a polar component related to the bonding forces between polar molecules. An increased forces between polar molecules. An increased polar component for the treated membrane can indicate improved membrane surface wettability [22, 23].

After UV treatment for 72 h, the polar component of the membrane surface increased from 4.1 mJ/m² for untreated to 49.1 mJ/m² and 56.6 mJ/m² for UV254 and UV312 treated membranes, respectively, shown in Figure 2B. So, for a long treatment time of up to 72 h, the hydrophilicity and surface energy of membranes treated with UV312 were better when treated with UV254. However, for short treatment times of less than 10 h, the hydrophilicity and surface energy with UV254 were better than with UV312. The hydrophilicity of PSF membrane surface may come from the hydroxyl groups that were confirmed by FTIR, as shown in Figure 3. The intensity of the hydroxyl (-OH) groups in FTIR results (3,100 – 3,600 cm⁻¹) was higher after UV312 treatment (dark blue line) than after UV254 treatment (orange line). The high-energy UV254 radiation may have destroyed formed -OH groups after 10 h of treatment. So, the membrane treated by UV254 has less OH on membrane surfaces than the membrane treated by UV312. The amount of polar functional groups on membrane surfaces contributed to hydrophilicity [1, 24]. So, the PSF membrane that was treated for 72 h with UV312 had the lowest WCA and the highest SE, and this matches the results from FTIR.

Although WCA of the treated membrane surface strongly decreased after treatment with UV, the WCA of so treated membrane gradually increased in a few hours, in other words the hydrophilicity of the membrane decreased. The membrane was reverting back to hydrophobic after the UV treatment. This behavior may be caused by the decay of free radicals or of free charges on the membrane surfaces, leading to a rearrangement of

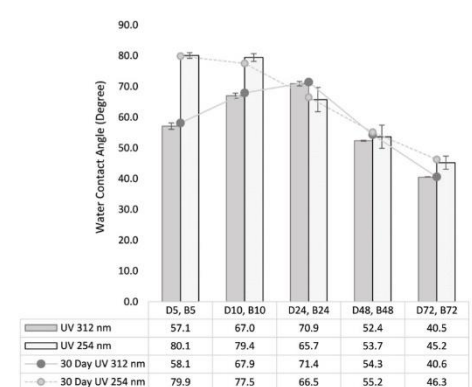


Figure 4 The water contact angles immediately after of PEG-UV treatment (bars) and 30 days later (lines)

the polar groups into the bulk material, or of nanopolar groups from the bulk to the surface, and migration of low molecular-weight oxidized materials (LMWOMs) from the surface to the bulk [25, 27]. The rapid return of the membrane surface to hydrophobic status becomes an important issue that devalues the UV-treatment. However, this drawback can be solved by PEG-grafting. PEG was grafted on an active membrane surface after the UV irradiation treatment (PEG-UV). The results in Figure 4 show that as treatment time was increased, the WCA of the treated membrane (PEG-UV) decreased. For PEG-UV254 (B5, B10, B24, B48, and B72) cases the WCA continued to decrease with treatment time, while for PEG-UV312 (D5, D10, D24, D48 and D72) cases the WCA pattern was different. With treatment times from 5 to 24 h (D5, D10, D24), the WCA increased, but with treatment times longer than 24 hours (D48, D72) the WCA decreased. This behavior may be caused by the broad wavelength spread of the UV light, as shown in Figure 1B. Although UV-254 provided lower WCA than UV-312 for treatment in a short period (less than 10 h), but for long period of treatment time (more than 10 h) UV-312 provided lower WCA than

UV-254. These results may cause by the prominent intensity of UV source. UV-254 has only one prominent peak while UV-312 has two prominent peaks (312 nm

and 360 - 370 nm) which shown the better results than UV-254 after treatment for more than 10 h shown in Figure 4.

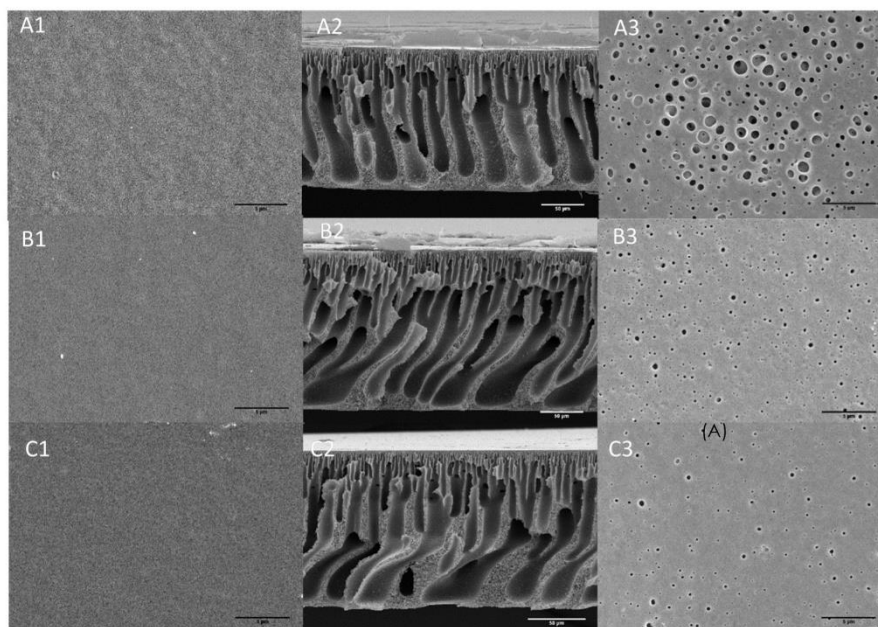


Figure 5 SEM images A1, B1, and C1 are of the top; A2, B2, and C2 of the cross section; and A3, B3, and C3 of the bottom of the membrane. Here A, B, and C are the D5, D24 and D72 conditions, respectively

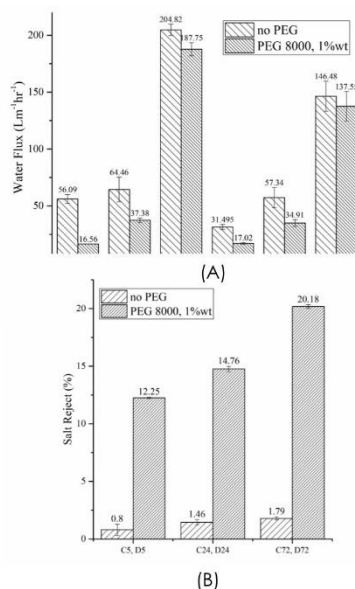


Figure 6 Water flux (A), and salt rejection (B) of PEG-UV treated membranes

However, both UV 254 nm and UV 312 nm treatments gave the lowest WCA with 72 h treatment, and PEG-UV312 (D72) case had a lower WCA than the PEG-UV254 (B72) case. Furthermore, the WCA of each treated membrane remained constant after 30 days from the completed membrane treatment. This means that PEG-UV combination can provide prolonged hydrophilicity to treated membranes, for at least 30 days after completion of the treatment. The PEG-UV312 approach uses high energy from UV light to cut hydrogen bonding (H-) from methyl side groups in the PSF membrane and reconstructs chemical bonds by grafting with PEG. On the other hand, the excess energy of UV 254 nm irradiation can destroy the structure of membrane surface, causing pore etching or polymer chain scission of the membrane [28, 29]. So, PEG grafting after UV 312 nm treatment was better than after UV 254 nm treatment. The FTIR spectra in Figure 3 show the C-O-C ether stretch peaks [1,30,31] at 1,100 – 1,300 cm⁻¹, and intensity of the light blue line (PEG-UV312 treatment, D72) is higher than that of the yellow line (PEG-UV254 treatment, B72). The intensity of C-O-C relates to the PEG functional groups. This means that the intensity of C-O-C can indicate the amount of

PEG on PSF membrane surface. The results in Figure 4 reveal that WCA after PEG-UV312 treatment was lower than after PEG-UV254 treatment, matching the FTIR results in Figure 3.

The morphologies of PEG-UV312 treated membranes after treatments for 5h, 24 h and 72 h (D5, D24, and D72) are shown in Figure 5. These show small pores on membrane surfaces due to the PEG adhered on the polymer component, and show similar morphologies for both top surface (A1, B1, and C1) and cross-section (A2, B2, and C2).

Although the pores are small, the water flux and salt rejection results improved with treatment time, as shown in Figure 6. This may be caused by improved hydrophilicity of the treated membrane surfaces, due to PEG grafting.

4.0 CONCLUSION

Hydrophilicity of a PSF membrane can be improved by UV irradiation, which can beneficially be followed by PEG grafting. The energy of UV light can break down chemical bonds on the PSF polymer membrane, so that polar functional groups are created on the membrane surface. Different UV wavelengths provide different photon energy levels, which affects the mechanisms and reactions on the membrane surfaces, leading to different surface wettability responses to treatment time. In addition, PEG grafting after the UV treatment was found to prolong hydrophilicity to last for at least 30 days after treatment. Furthermore, membrane improved by PEG-UV treatment provided high permeability and selectivity at the same time, which is attributed to the polar functional groups of PEG on the treated membrane surfaces.

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CHAPTER 4

PAPER II

Thailand is the world's biggest producer and exporter of natural rubber. Unfortunately, the production of latex and the processing of rubber results in foul smells and effluent, which have a negative impact on the environment. Because of the unusable components in the remaining fraction (NR serum) from the chemical processing of rubber latex, which consists of many organic compounds, membrane technology is one of the wastewater treatment techniques that do not degrade organic molecules. However, the membrane filtration of NR serum has been proved challenging because the serum contains minute residual rubber particles that are sticky and easy to clog the membrane, blocking pores and causing irreversible fouling. A high-efficiency technique to reduce the membrane fouling is the modification membrane to hydrophilicity on the membrane surface. So, in this work focuses on modification of the membrane surfaces by electron beam irradiation and sodium styrene-sulfonate (SSS) grafting for anti-fouling of NR serum separation. X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), Water contact angles (WCA), surface energy (SE), scanning electron microscopy (SEM), and atomic force microscopy (AFM) were used to evaluate the surfaces of the modified membrane. Bovine serum albumin (BSA) and NR serum were used to test filtration performance. After acrylic acid and sodium styrene-sulfonate (AAc/SSS) grafting, a membrane irradiated at 10 MeV and 50 kGy had the greatest hydrophilicity. This membrane showed high flux recovery ratios after 2nd cycle of BSA and NR serum filtrations. Moreover, total solid content (TSC) and total protein rejection rates in NR serum were high percentages.

PAPER II

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E-beam induced grafting of binary monomer on polysulfone membrane for the separation of skim natural rubber latex

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ABSTRACT

Polysulfone (PSF) membranes containing TiO₂ were prepared by phase inversion. The membrane surfaces were modified by electron beam irradiation at energies of 3 and 10 MeV for irradiation doses of 10 and 50 kGy. Hydrophilic sulfonate groups were then introduced by single-step grafting using a binary monomer of acrylic acid (AAc) and sodium styrene-sulfonate (SSS). The surfaces of the modified membranes were characterized by analysis of water contact angles (WCA), surface energy (SE), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and scanning electron microscopy (SEM). Filtration performances were evaluated using bovine serum albumin (BSA) and NR serum. A membrane irradiated at 10 MeV and 50 kGy showed the highest hydrophilicity after AAc/SSS grafting, with a WCA of 35.2 degrees and SE of 60.1 mJ/m². After 2nd cycle filtrations of BSA and NR serum, this membrane demonstrated flux recovery ratios of 97.8% and 95.9%, respectively. The rejection rates of total solid content (TSC) and total protein in NR serum were 72.1% and 91.5%, respectively.

1. Introduction

Thailand is the world's biggest producer and exporter of natural rubber (*Hevea brasiliensis*) [1]. Total rubber production in Thailand in 2018, 2019, and 2020 was 4.81, 4.77, and 4.24 million metric tons, respectively (Department of International Trade Promotion, Ministry of Commerce, Thailand, <https://www.ditp.go.th.com>, 2021) [2]. Unfortunately, latex production and rubber processing causes environmental issues from foul odors and wastewater [3]. Because the chemical processing of rubber extracts the usable rubber particles in natural rubber latex, the wastewater from the process contains the unusable components in the remaining fraction (NR serum) [4]. NR serum contains water, proteins, resins, sugars, ash, fats, residual rubber particles, and other compounds [5]. Value could be added to the large quantity of NR serum produced in several countries by treating the serum to extract amino acids, proteins and other elements [6].

Wastewater from rubber processing can be treated by organic separation techniques such as coagulation and activated sludge but the application of these treatments has been limited by costs, complicated

separation equipment, low removal efficiency, and organic molecule degradation [7]. Consequently, membranes, which do not degrade organic molecules, present a more viable solution to the problem of separating NR serum from water. However, the membrane filtration of NR serum has proved challenging because NR serum contains small residual rubber particles that are sticky and tend to clog the membrane, obstructing pores and leading to irreversible fouling [8,9]. Fouling is a crucial factor in membrane performance and can be influenced by electrostatic interactions, hydrogen bonding effects, hydrophobicity, and Van der Waals forces [10]. One way to reduce the accumulation of hydrophobic rubber molecules is by improving the hydrophilic properties of the membrane surface [9,11], which is the most critical factor in anti-fouling.

Increasing the hydrophilicity of a membrane surface reduces the adsorption of hydrophobic molecules at the membrane [12] but unfortunately, most polymer membranes are naturally hydrophobic. Polysulfone (PSF), for instance has excellent mechanical stability, high chemical and thermal resistance but has a low surface energy and is therefore hydrophobic [13]. Since membrane substrates should be as

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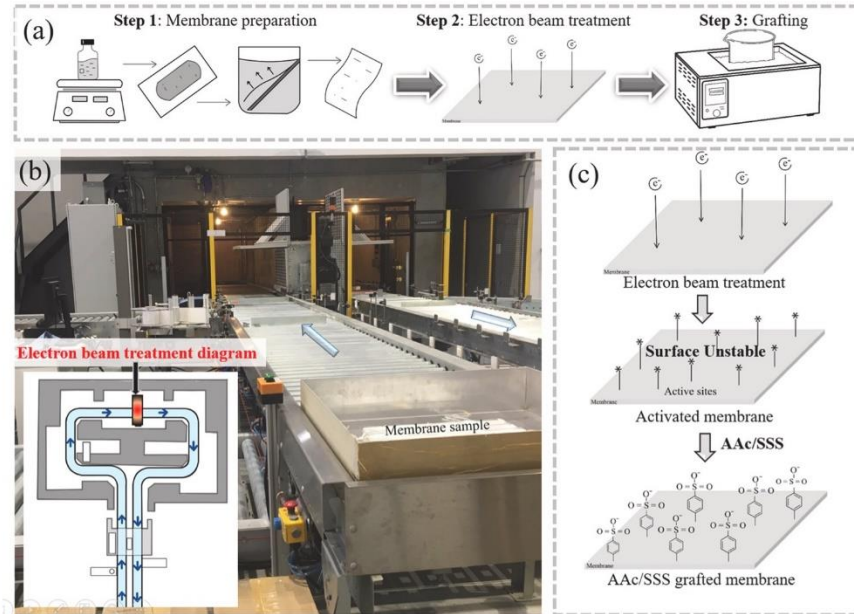


Fig. 1. Diagram (a) shows the grafting method, illustration (b) shows the electron beam treatment equipment and diagram (c) shows the grafting method.

Table 1
Sample labels of the electron treatment condition with AAc/SSS grafting.

Energy (MeV)	Dose (kGy)	
	10	50
3 MeV	PSF-A	PSF-B
10 MeV	PSF-C	PSF-D

membranes before e-beam treatment and ungraft AAc/SSS.

2.4. Surface characterization

The degree of grafting (%DOG) was calculated based on the weight increase of the sample, using Eq. (1) [19,27];

$$\%DOG = \left(\frac{W_g - W_0}{W_0} \right) \times 100 \quad (1)$$

where the W_g is the weight of the membrane after grafting and W_0 is the initial weight of the membrane before grafting.

The surface chemical composition of grafted PSF membranes was studied by Fourier transform infrared spectroscopy (FTIR, Tensor 27, Bruker, USA) and X-ray photoelectron spectroscopy (XPS, AXIS Ultra DLD, Krotos, Analytical Ltd. UK). To measure the water contact angle (WCA) and surface energy (SE), a contact angle measuring instrument (Model OCA 15 EC, Data Physics Instruments GmbH, Germany) was used. The contact angles of water, formamide, and ethylene glycol were used to analyze the SE of the membrane by the Owens-Wendt model, shown in Eq. (2) [34];

$$\gamma_{LV}(1 + \cos\theta) = 2(\gamma_L^d \cdot \gamma_S^d)^{1/2} + 2(\gamma_L^p \cdot \gamma_S^p)^{1/2} \quad (2)$$

where γ^p is the polar component (mJ/m^2), γ^d is the dispersive component (mJ/m^2), θ is the contact angle (degree), and γ_{LV} is the free energy

of the liquid and vapor (mJ/m^2).

Surface morphologies were observed by atomic force microscope (AFM, Nanosurf easyscan2 flex, Switzerland) and scanning electron microscope (SEM, Quanta400, Thermo Fisher Scientific, USA).

2.5. Evaluation of membrane performances

2.5.1. Permeation and separation of membrane

The permeation and separation properties of the membranes were tested in two steps. In the initial step, the water flux, BSA flux, and BSA rejection of all membranes were tested in a dead-end system, to find the best membrane condition. In the second step, the membrane that performed best in the first step and the untreated membrane were tested to compare fouling behavior during NR serum filtration in a cross-flow system, following Sirinpong et al. [31].

Pure water flux and BSA solution flux were determined through a dead-end filtration cell at room temperature with an effective membrane area of 14.6 cm^2 . The dead-end cell was driven by nitrogen gas at a pressure of 0.3 MPa. The flux of the membrane ($J, \text{Lm}^{-2}\text{h}^{-1}$) was determined according to Eq. (3) [35,36];

$$J = \frac{V}{A \times t} \quad (3)$$

where V is the volume of the filtrate (L), A is the effective area of the membrane (m^2) and t is the testing time (h). The membrane rejection ratio (R) of 1.0 gL^{-1} BSA-Tris solution (pH 7.4) was calculated using Eq. (4) [13];

$$R(\%) = \left(1 - \frac{C_p}{C_f} \right) \times 100 \quad (4)$$

where C_p and C_f (g L^{-1}) refer to the concentrations of BSA in permeate and feed solutions, respectively. The concentration of BSA was measured by UV-vis spectrophotometer (U-2900/2910, Japan) at 280 nm [37].

hydrophilic as possible, the hydrophilicity of PSF membranes must be increased if they are to be effective.

Several methods of improving membrane surfaces have been investigated and antifouling characteristics have been significantly improved by grafting hydrophilic groups onto the membrane surface. Rana et al. [14,15] modified polyethersulfone (PES) membranes by blending with a hydrophilic surface modifying macromolecule (LSMM). The modified membranes showed higher hydrophilicity and fouling resistance due to the electrostatic interactions and surface free energy of the modified membrane surface. Kusworo et al. [7] doped PSF membranes with titanium dioxide (TiO₂) to enhance their hydrophilicity, and higher flux and flux recovery were achieved with the doped membranes. TiO₂ nanoparticles have been widely studied due to their high stability, specific morphology and low toxicity [16].

Physical techniques such as UV irradiation and plasma treatment are also popular methods of improving membrane surfaces. UV irradiation is inexpensive but takes a long time to implement [17]. Low-pressure plasma treatment is highly efficient but the required low-pressure system limits the size of membrane that can be treated and takes a long time to develop the necessary pressure [18]. One highly efficient alternative is electron-beam (e-beam) irradiation. This technique does not use the expensive vacuum equipment required for conventional low-pressure plasma treatment. Since the process is simple and inexpensive large-scale industrial applications are possible [19]. The electron-induced mechanism can be briefly explained as follows. When polymer molecules are activated by ionizing radiation, the electrons induce chain scissions and hydrogen abstractions in the polymer chains, and as a result, free radicals are created [20–22]. Radicals produced by the cleavage of carbon-hydrogen bonds are extremely unstable and quickly disappear, resulting in cross-linking or recombination with other monomers, whereas chain-end radicals formed by the cleavage of main chain carbon-carbon bonds may be present in small amounts [23,24].

Using e-beam irradiation, Xi et al. [19] introduced hydrophilic groups onto a membrane surface and studied the effect of monomer concentration and e-beam irradiation dose. A binary monomer of sodium styrene-sulfonate and acrylic acid (AAc/SSS) was grafted and the grafted polymer increased the hydrophilicity of the membrane. Wang et al. [25] investigated the surface modification of polytetrafluoroethylene (PTFE) membranes with AAc/SSS and tested the anti-fouling properties of the modified membrane against bovine serum albumin (BSA) protein. The wettability of the membrane and electrostatic repulsion between the membrane surface and the BSA produced improved antifouling characteristics.

The sulfonate group has been used in many fields, including biomedical and electrical applications [26]. Sodium styrene-sulfonate (SSS), a hydrophilic monomer with an SO₃⁻ group, has good antifouling properties due to its hydration sphere and high electrostatic force [19,27], but cannot be directly grafted into a hydrophobic membrane surface because of the incompatibility of the highly ionized and hydrophilic SO₃⁻ group [28]. However, SSS has been successfully grafted onto various polymeric membranes with the aid of acrylic acid (AAc) [29,30]. AAc grafted onto a polymer membrane has previously improved compatibility between the membrane and SSS [19,27]. Therefore, this research focuses on using e-beam energy to assist AAc/SSS grafting, which has not been frequently reported. This study then investigated the antifouling property of the modified membrane during NR serum filtration.

The grafting of the binary AAc/SSS monomer on the polysulfone (PSF) membrane was induced by e-beams with energies of 3 and 10 MeV used to impart irradiation doses of 10 and 50 kGy. The effects of the different irradiation treatments on the hydrophilicity of the modified membrane surface were investigated. Water contact angle (WCA), surface energy (SE), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), atomic force microscope (AFM), and scanning electron microscopy (SEM) were used to investigate the properties of the membrane. After characterization, the modified

membrane was used to filter BSA and NR serum, and the flux, fouling behavior, flux recovery, anti-fouling and rejection properties of the modified membrane surface were evaluated.

2. Experiments

2.1. Materials

Polysulfone (PSF) Udel P-1700 was supplied as pellets by Solvay (China). Titanium dioxide (TiO₂; 32 nm APS powder MW. 79.90) nanoparticles were supplied by Alfa Aesar (United States). Acrylic acid (AAc, 98%) was from Acros organics (Belgium). N-Methyl-2 pyrrolidone (NMP), sodium styrene-sulfonate (SSS, >90%), polyvinylpyrrolidone (PVP, K30, Mw 40,000), Tris (hydroxymethyl) amino-methane (99.9%) and bovine serum albumin (BSA, Mw 66 kDa) were from Sigma-Aldrich (USA). Sodium hydroxide pellets (NaOH, 98%) were supplied by Loba Chemie (India). Hydrochloric acid (HCl, 36.5–38.0%) was from J.T. Baker (Thailand). Formamide and pure ethylene glycol were supplied by POCH (Poland).

2.2. Preparation of PSF membranes

The membrane was prepared by a phase inversion method [17]. A TiO₂-doped solution was first prepared using 0.5 wt% PVP and 81.0 wt % NMP mixed under magnetic stirring for 10 min in a beaker, after which 1 wt% TiO₂ was added and stirring continued until a homogenous mixture was obtained. The doped solution was completed by adding 17.5 wt% PSF under vigorous stirring, which continued until homogeneity was achieved [17,31]. The homogenous solution was then sonicated using an ultra-sonicator (GT SONIC, VGT-1620 T) for 60 min to remove any bubbles. The solution was cast on a clear glass plate with a thickness of about 200 μm [32]. The cast solution was left in the ambient conditions for 60 s (evaporation time) before being immersed on the glass plate in a water bath. The PSF membrane was then peeled off the glass, placed in a second water bath and soaked to remove any solvent. Before surface modification, the membrane was left to dry in the ambient conditions for 24 h and finished in a vacuum oven at 70 °C for 24 h. This membrane was labeled PSF/TiO₂. A second solution was prepared by the same procedure, without TiO₂, using 0.5 wt% PVP, 82.0 wt% NMP and 17.5 wt% PSF. This membrane was labeled PSF/No-TiO₂. The process of membrane grafting is illustrated in Fig. 1 (a).

2.3. Grafted copolymerization of PSF with AAc/SSS

Using a high-energy electron beam accelerator (Mevex Corporation Ltd., MB 20–16, Canada) at the Thailand Institute of Nuclear Technology (Public Organization), the prepared PSF membranes were irradiated with beam energy (Fig. 1(b)). The energy and dose of radiation have different impacts on different membrane surfaces. However, our e-beam source has some limitations. The lowest e-beam energy that could be applied was 3 MeV but the use of a high e-beam energy and high radiation dose can cause polymer cracking, which has been shown to result in considerable mass loss [22,33]. In this study, the impact of e-beam energy and radiation dose on AAc/SSS grafting and hydrophilicity was examined at 3 MeV with doses of 10 kGy and 50 kGy, and at 10 MeV also with doses of 10 kGy and 50 kGy. Using this process, the maximum width of membrane that can be treated is 0.8 m, while the length is theoretically unlimited. The process of irradiation-grafting is depicted in Fig. 1(c). After irradiation, the PSF membranes were placed in a container of AAc/SSS mixed at a ratio of 5:1 [19]. The container was sealed and heated at 70 °C for 24 h. After heating, the membrane was removed, rinsed with ethanol and then immersed in water at 50 °C for 24 h to remove homopolymer [19,27]. Finally, the modified PSF membrane was dried overnight at 60 °C in a vacuum oven. The modified membrane labels are shown in Table 1. PSF-O denotes the PSF/TiO₂

2.5.2. Fouling behavior and skim natural rubber latex (NR serum) separation

The permeation performance and antifouling properties of the membrane were evaluated against a BSA solution (1 gL^{-1} of BSA in Tris-HCl, pH 7.4) and NR serum. The solutions were passed at room temperature through a cross-flow filtration cell with an effective membrane area of 28.0 cm^2 . The experimental set-up consisted of a membrane cell, a feed tank, a diaphragm pump, valves, and pressure gauges (Fig. 2). All filtration experiments were applied using a pressure of 0.3 MPa, weights were measured by digital balance (Adam, Highland: HCB1002, USA), and flux was calculated from Eq. (3) [38].

Skim natural rubber latex (NR serum: 5.85%wt of total solid content, 4.73%wt of total protein) was obtained as waste from the creaming process of natural rubber collected from RRIT251 clones of *H. brasiliensis*. Processing was carried out at the Rubber Product and Innovation Development Research Unit, Prince of Songkla University. The rejection performances of the membranes were determined from the total solid content (TSC) and total protein concentration in NR serum. The TSC was determined by coagulation. Total protein was measured with a CN analyzer (CN628, USA) using a combustion method.

Before starting the experiments, each membrane was compacted with water at 0.4 MPa for around 30 min to get a steady flow. The operating pressure was then reduced to 0.3 MPa for 1 h to arrive at the initial pure water flux (J_{w1}), which was measured every 10 min and used for all experiments [13,36]. Three cycles of experiments were then carried out. In each cycle, BSA or NR serum solution was filtered for 10 h. After the filtration of the first cycle, the membrane was washed with water for about 30 min, followed by chemical cleaning with 0.5% NaOH for 30 min [39] (washing time was not included in the filtration cycle). BSA flux (J_p), and NR serum flux (J_{NR}) were monitored for 10 h in each cycle. Pure water flux was measured within 60 min of cleaning the membrane after the first cycle and was recorded as J_{w2} [37]. The direct measurement of the permeate volume and estimation using Eq. (3) were

used to determine each flux (J_w , J_p , and J_{NR}) of the membrane. The rejection of TSC, total protein of NR serum and BSA were calculated using Eq. (4). Several parameters were used to investigate the antifouling properties of the membranes during filtration. Eqs. (5–8) were used to calculate the flux recovery ratio (FRR), total fouling ratio (R_t), reversible fouling ratio (R_r), and irreversible fouling ratio (R_{ir}) [13,36,37]:

$$FRR_i(\%) = \left(\frac{J_{w,i}}{J_{w,i-1}} \right) \times 100 \quad (5)$$

$$R_t(\%) = \left(\frac{J_{w1} - J_{p, NR}}{J_{w1}} \right) \times 100 \quad (6)$$

$$R_r(\%) = \left(\frac{J_{w2} - J_{p, NR}}{J_{w1}} \right) \times 100 \quad (7)$$

$$R_{ir}(\%) = \left(\frac{J_{w1} - J_{w2}}{J_{w1}} \right) \times 100 = R_t - R_r \quad (8)$$

3. Results and discussion

3.1. Membrane characterization and properties

The untreated and ungrafted PSF/TiO₂ membrane produced a lower WCA and higher polar component of surface energy than the untreated and ungrafted PSF/No-TiO₂ membrane (Table 2). Therefore the hydrophilicity of the PSF/TiO₂ membrane was greater. The enhanced hydrophilicity of the PSF/TiO₂ membrane derived from the naturally hydrophilic nanoparticles of TiO₂ [7]. After AAC/SSS grafting of the membranes without e-beam treatment, the %DOG of the PSF/TiO₂ membrane was only slightly higher than the %DOG of the PSF/No-TiO₂ membrane. Also, the %DOG of both AAC/SSS-grafted membranes was low without e-beam treatment. Therefore, we concluded that TiO₂ hardly affected the grafting process. These results are also consistent with the results reported by Xi et al. [19], so the PSF/TiO₂ was the substrate membrane used in the rest of this study.

The effects of energy and radiation dose conditions on the %DOG, WCA and SE of the PSF/TiO₂ membrane were examined. At the same dose, an e-beam energy of 10 MeV (PSF-C, PSF-D) had a greater impact than 3 MeV on the %DOG (Fig. 3 (a)). When the effect of radiation dose was studied, 50 kGy (PSF-B, PSF-D) radiation dose resulted in a higher %DOG than 10 kGy (PSF-A, PSF-C). Higher energy and irradiation doses resulted in higher %DOG because more intense and repetitive surface interactions resulted in more surface activation [28].

The WCA was measured after AAC/SSS grafting of various e-beam treated membranes. The membrane surface treated with the higher energy of 10 MeV and higher dose of 50 kGy before AAC/SSS grafting (PSF-D) produced the lowest WCA (Fig. 3 (b)). The WCA of PSF-D was 35.2 degrees compared with 85.4 degrees for PSF-O. The hydrophilicity indicated by the WCA corresponded to the %DOG value of PSF-D. Water molecules are attracted by higher SE, resulting in a lower WCA. SE consists of two components, the polar component and the dispersive component. The relationship is shown in Eq. (2). The surface energy of polar molecules is represented by the polar component, whereas the surface energy of non-polar components is represented by the dispersive component [40,41]. The SE of the membranes was determined using Eq. (2). The enhanced hydrophilicity of the membrane surface was mostly attributable to an increase in the polar component. The SE of PSF-D was the highest (60.1 mJ/m^2) and the SE of PSF-O (the untreated membrane) was the lowest (29.2 mJ/m^2). The polar component of PSF-D was 44.2 mJ/m^2 , up from 6.1 mJ/m^2 for PSF-O, and the dispersive component was 15.9 mJ/m^2 , down from 23.1 mJ/m^2 (Fig. 3(c)). The increase in SE was thus confirmed by the enhancement of the polar component. Therefore, the PSF-D membrane was the most hydrophilic of all the membranes tested. This conclusion was substantiated by the WCA and

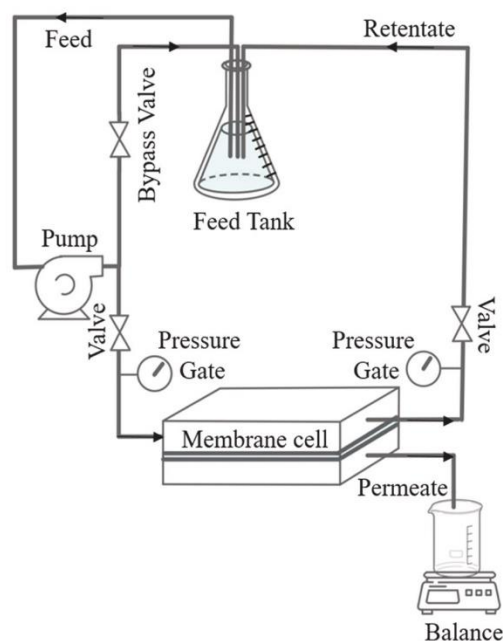


Fig. 2. Schematic diagram of lab-scale cross flow filtration set-up.

Table 2

The degree of grafting (DOG (%)), water contact angle (WCA (degree)), and surface energy (mJ/m^2) of the ungrafted and AAC/SSS-grafted PSF/No-TiO₂ and PSF/TiO₂ membranes before e-beam treatment.

Membrane	Grafting	DOG (%)	WCA (degree)	Surface Energy (mJ/m^2)		Label
				Dispersive component	Polar component	
PSF/No-TiO ₂	–	–	96.6 ± 3.1	38.1 ± 4.4	0.7 ± 0.1	–
PSF/TiO ₂	AAC/SSS	1.45 ± 0.40	90.1 ± 0.8	33.3 ± 1.8	2.3 ± 0.4	–
	AAC/SSS	1.51 ± 0.41	80.7 ± 0.4	27.3 ± 1.0	6.1 ± 0.2	PSF-O

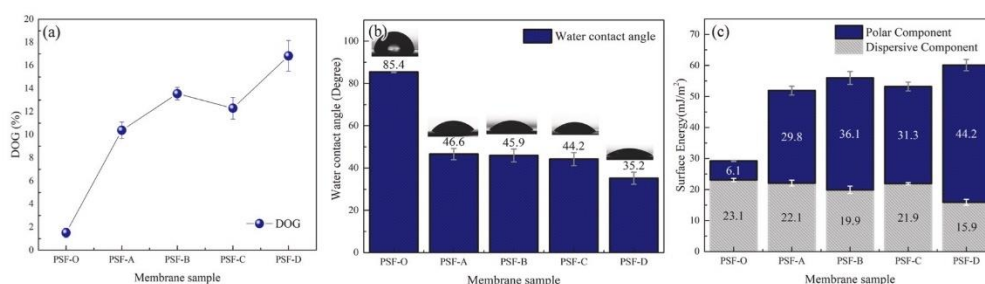


Fig. 3. Degree of grafting (a), water contact angle (b), and surface energy (c) of the untreated and treated membranes.

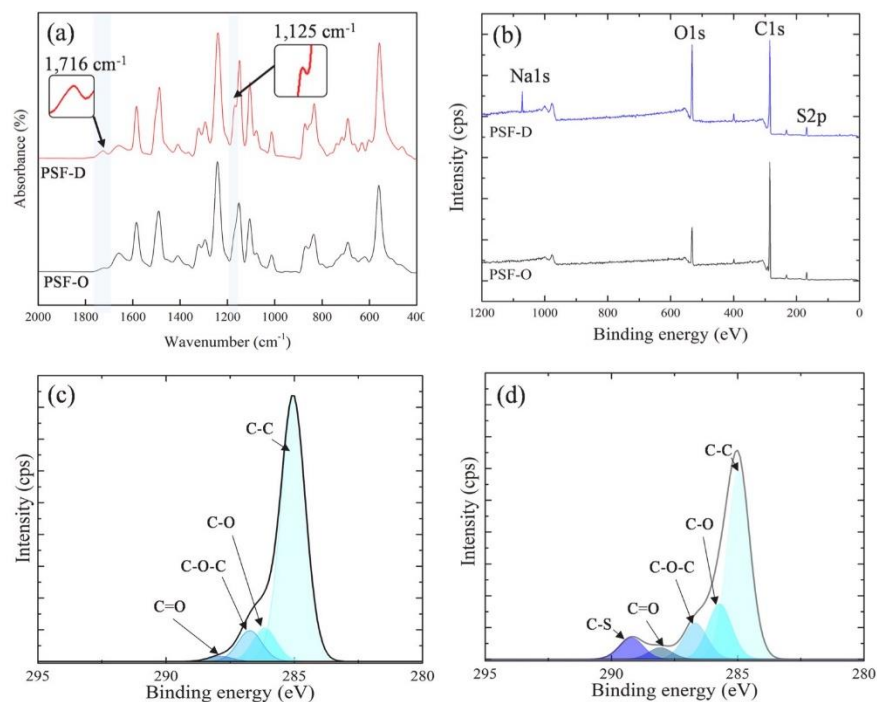


Fig. 4. FTIR spectra (a) are of the untreated membrane (PSF-O) and the membrane treated with 10 MeV, 50 kGy + AAC/SSS (PSF-D). XPS survey-scans (b) are of the investigated membranes. The C1s spectra of the PSF-O (c), and the PSF-D (d) show differences the formation of a new group.

SE data, and further experiments in this study focused on a comparison of the properties of the PSF-D membrane and the PSF-O membrane.

In the FTIR spectra of PSF-O and PSF-D (Fig. 4(a)), the carbonyl group (C=O) of PSF-D was detected at 1716 cm^{-1} . The presence of this group on the surface of the PSF-D membrane but not on the surface of PSF-O indicates that C=O determined membrane hydrophilicity [19]. The detection of $-\text{SO}_3^-$ at 1125 cm^{-1} [27] in the spectrum of PSF-D confirms the presence of a new functional group on the membrane surface after grafting with AAc/SSS. This result demonstrates that SSS polymer chains were successfully grafted onto the membrane surface [20,30].

In the XPS survey spectra of the PSF-O and PSF-D membranes (Fig. 4(b)), the binding energies of C 1 s, O 1 s, and Na 1 s are detected at 285, 532, and 1071 eV, respectively [39,42]. The intensity of O 1 s is higher in the PSF-D spectrum than the PSF-O spectrum, but the intensity of C 1 s is lower (Table 3). The increase in oxygen content and the decrease in carbon content are elucidated by the C 1 s spectra (Fig. 4(c) and 4(d)). In the spectrum of the PSF-D membrane, C-C (284.8 eV) decreased, whereas C-O (286.1 eV), C-O-C (286.7 eV), and C=O (287.9 eV) increased, and C-S (289.2 eV) appeared as a new group [27,39,43,44]. A bond transition possibly occurred on the membrane surface, C-C being destabilized by electron beams and then forming new bonds with O and S. Moreover, the presence of SSS is indicated by an increase in Na 1 s (1071.5 eV), S 2p (168.0 eV) [42,43], and C-S re-bonding on the PSF-D membrane surface. S 2p mass concentration was 6.33% for PSF-D compared to 5.66% for PSF-O (Table 3). The hydrophilic functional groups of the PSF-D membrane increased when oxygen functions and SSS were enhanced [27,39]. The XPS results are consistent with the FTIR analysis.

The morphologies of PSF-O and PSF-D were observed by AFM and SEM. The roughness of the surface of the PSF-O membrane was 34.05 nm and the roughness of PSF-D was 108.49 nm (Fig. 5(a-d)). The increased roughness was most probably an effect of the electron beam irradiation and the binary monomer molecule (AAc/SSS). The result is consistent with the report of Fu Liu et al. [27], who observed an increase in surface roughness after using an e-beam to activate a poly (vinylidene fluoride) surface for the grafting of AAc/SSS. The SEM images of the membrane surfaces reveal slight differences between the two membranes. The PSF-O membrane is smoother than the PSF-D membrane (Fig. 5(e, g)). The high electron beam energy and high dose degraded the surface of PSF-D and created fissures [45]. Although the energy and dose of the electron beam degraded the membrane surface, the internal structure of the membrane was not affected by the energy and dose of the e-beam (Fig. 5(f, h)) and the higher energy and bigger dose resulted in improved grafting and hydrophilicity (Fig. 3). Using a 10 MeV electron beam with a 50 kGy dose induced better grafting of the AAc/SSS and increased the hydrophilicity of the PSF membrane surface.

3.2. Separation performances

Water flux and BSA protein rejection were studied by dead-end filtration. The experiment investigated the performances of PSF-O, PSF-A, PSF-B, PSF-C, and PSF-D membranes. E-beam activation at higher energy and/or higher dose produced a membrane that allowed greater water flux. The water flux of PSF-O was the lowest (0.29 LMH/bar) and the water flux of PSF-D was the highest (1.36 LMH/bar) (Fig. 6). BSA protein flux was also lowest for PSF-O (0.24 LMH/bar) and

highest for PSF-D (0.61 LMH/bar). The increased flux was associated with the higher hydrophilicity and surface energy of the membrane, as hydrophilicity attracts water molecules to pass through the membrane. BSA protein rejection decreased when the energy and/or dose of the e-beam was high. However, the increase in flux was more pronounced than the decrease in the rejection ratio. The results of the study indicate that the PSF-D membrane was more effective at separating BSA than the other tested membranes.

The membrane fouling behaviors of the PSF-O and PSF-D membranes were studied comparatively by cross-flow filtration over three cycles of BSA protein and NR serum, using the set-up illustrated in Fig. 2. In the first cycle, the initial significant permeate flux through the PSF-O quickly declined due to the hydrophobicity of the membrane (Fig. 7(a)). The organic compounds readily accumulated on the hydrophobic membrane surface, especially during NR serum separation. Flux through PSF-D was high at the beginning and declined only slightly due to the effect of the hydrophilicity of the PSF-D membrane, which reduced the accumulation of molecules on the membrane surface [25]. Flux through the PSF-D during protein separation constantly decreased due to the increased deposition of organic compounds. However, at the end of the first cycle, flux through PSF-D was still higher than flux through PSF-O. BSA was used as the model protein for investigating membrane anti-fouling and recycling properties. The decrease in flux through the PSF-D membrane was greater than the decrease in flux through the PSF-O membrane because the greater flux increased deposition. However, after 600 min of filtration, the flux through PSF-D was still higher than the initial flux through PSF-O (Fig. 7(b)). The three cycles displayed the same profiles. Membrane fouling reduced flux during the filtration process as rejected protein molecules adsorbed and accumulated on the surface and inside the pores of the membrane, reducing permeability [37]. The hydrophilic properties of the PSF-D membrane surface exerted an electrostatic force between the surface and the protein molecules, resulting in greater flux and less deposition on the membrane surface. The experiment was a long-term dynamic process over three cycles in which the membrane was washed after the first cycle. When re-tested after washing, the flux through the PSF-D membrane returned to a high level and then gradually declined as before.

NR serum contains a variety of components that include carbohydrates (quebrachitol, sucrose, glucose, and fructose), lipids, organic acids, inorganic anions, metallic ions, and rubber particles (cis-1,4-polyisoprene rubber, particle size 0.15–3 μm), which are the main cause of membrane fouling, owing to their sticky nature [46]. NR serum also contains a variety of proteins (α -globulin, Hevein, and others) with molecular sizes ranging from 14.4 to 116 kDa [47]. Consequently, anti-fouling properties like hydrophilicity and electrostatic interactions can significantly improve membrane properties. The NR serum fouling behavior of the PSF-O membrane exhibited a quick drop in flux during the first 200 min before progressively decreasing more gradually (Fig. 7(c)). The flux through PSF-D decreased gradually to the end of each cycle. After membrane cleaning at the end of the first cycle, flux through PSF-D began at a level close to the level exhibited at the beginning of cycle 1, but flux through the PSF-O membrane recovered less after each cycle.

The flux recovery ratio (FRR), total fouling ratio (R_t), reversible fouling ratio (R_r), and irreversible fouling ratio (R_{ir}) of the second cycle were calculated from Eqs. (5–8). The FRR calculated for the 2nd cycle was used to reflect membrane fouling resistance. The PSF-D membrane had a higher FRR than the PSF-O membrane for both BSA protein and NR serum filtration. The FRR of PSF-O was 90.9% for BSA protein and 79.8% for NR serum, while the FRR of PSF-D was 97.8% for BSA protein and 95.9% for NR serum (Fig. 8(a, b)). The 3rd cycle FRR of the PSF-D membrane was also greater than the 3rd cycle FRR of the PSF-O. The results demonstrate that organic molecules were adsorbed and deposited less on the PSF-D membrane than on the PSF-O membrane and were more easily removed from PSF-D because they did not adhere so well. The total fouling ratio (R_t), which is separated into the reversible fouling

Table 3
Chemical compositions (%) of the PSF-O and PSF-D membranes were derived from the XPS spectra.

Sample	%Mass Conc.				
	O 1 s	N 1 s	C 1 s	S 2p	Na 1 s
PSF-O	11.54	1.91	80.89	5.66	0.00
PSF-D	22.98	3.32	63.57	6.33	3.80

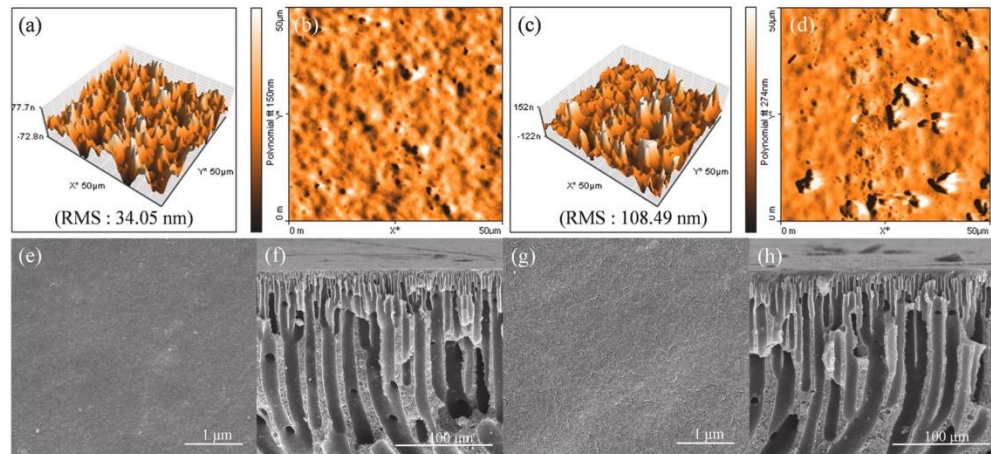


Fig. 5. AFM images of PSF-O (a, b) and PSF-D (c, d) membranes, SEM images of the morphology of PSF-O (e, f) and PSF-D (g, h) membranes: the surface images (e, g) are at $\times 30,000$ and the cross-section images (f, h) are at $\times 500$.

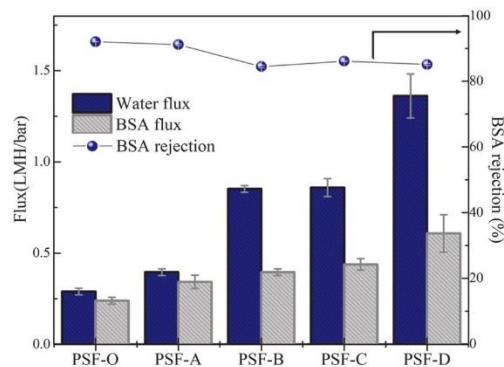


Fig. 6. Pure water flux, BSA flux, and BSA rejection at the untreated and treated membranes.

ratio (R_t) and irreversible fouling ratio (R_{ir}), can be used to quantitatively evaluate the antifouling property of membranes [37]. The R_t was predominantly the result of loose organic and inorganic adsorption on

the membrane surface, whereas the R_{ir} was the result of organic and inorganic deposition on the membrane surface or entrapment within the pores [48,49]. The R_t of PSF-O was 23.5% for BSA protein and 36.7% for NR serum, which are higher than the R_t of the PSF-D membrane in both cases (Fig. 8 c, d).

A greater R_t value indicates a higher overall flux loss, which translates to more protein adsorption and deposition on the membrane surface. Meanwhile, the R_{ir} values for the PSF-O were also higher than R_{ir} values for the PSF-D membrane. It was concluded that cleaning the PSF-O membrane could not remove the extreme fouling. The hydrophobicity of the membrane surface combined with the hydrophobic rubber molecules induced rubber particle deposition on the membrane surface and eventual penetration inside the pores, causing the higher R_{ir} . On the other hand, since the PSF-D membrane is hydrophilic, electrostatic interactions and the hydration sphere of the AAc/SSS grafting monomer repel hydrophobic molecules. As a result, the adsorption of rubber molecules was reduced, and there was less penetration into the pores (Fig. 9) [25,27,35].

On the 3rd cycle, the protein and NR serum FRRs of the PSF-O were reduced (Fig. 8 (a, b)) even though the membrane had been cleaned. Because the R_t and R_{ir} of the PSF-O were relatively high, FRR was relatively low in the 2nd and 3rd cycles. The protein and NR serum filtration of the PSF-D, on the other hand, remained relatively unchanged. The enhanced hydrophilicity of the membrane surface and the

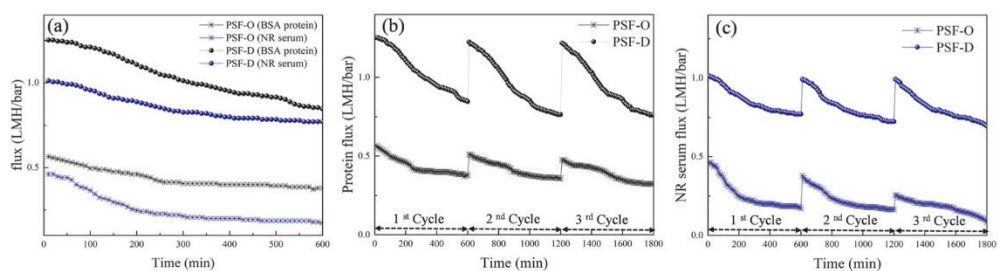


Fig. 7. The anti-fouling properties of the untreated PSF-O membrane and the PSF-D membrane were investigated in a cross-flow filtration experiment over three cycles. The charts show the permeate flux decay of the 1st cycle (a) and the fouling behavior of BSA protein (b) and NR serum (c).

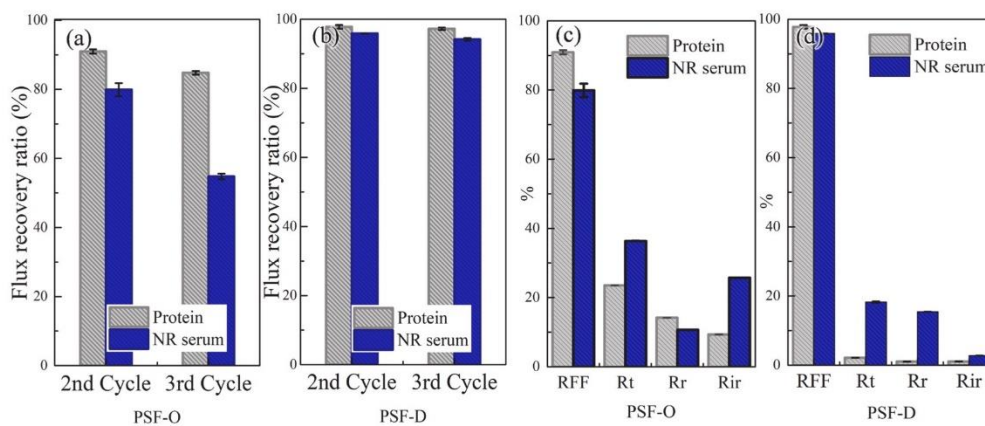


Fig. 8. The charts show the flux recovery ratios (FRR) of PSF-O (a) and PSF-D (b) membranes in the second and the third experimental cycles, and summarize the flux recovery ratios (RFF), total fouling ratios (R_t), reversible fouling ratios (R_r), and irreversible fouling ratios (R_{ir}) of PSF-O (c) and PSF-D (d) membranes during BSA protein and NR serum filtration experiments.

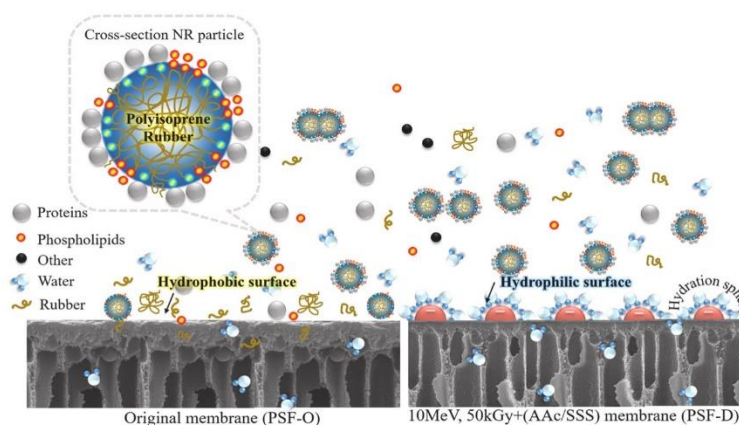


Fig. 9. Schematic representation of NR serum anti-fouling on the membrane.

electrostatic force from the polar functional groups contributed to the high percent FRR of PSF-D in both filtration experiments. This behavior was supported by the WCA, SE, FTIR, and XPS analyses. The result was improved anti-fouling. The PSF-D membrane demonstrated better anti-

fouling behavior than the PSF-O membrane and is more suitable for the intended use with NR serum.

According to the literature, the anti-fouling performance of a membrane is greatly impacted by its surface properties. Previous research

Table 4
Performances of various membranes reported in previous research.

Membrane	Treatment	Grafting	WCA (Degree)	Filtration	FRR (%)	Ref.
PSF-TiO ₂	E-beam	AAc/SSS	35.2	BSA protein	97.8 (2nd cycle) 97.2 (3rd cycle)	This work
PSF-TiO ₂	E-beam	AAc/SSS	35.2	NR serum	95.9 (2nd cycle) 94.2 (3rd cycle)	This work
PSF	UV	HBO	21.3	BSA protein	82.80	[13]
PTFE	-	AAc/SSS	Below 80	BSA protein	~90-100	[25]
PSF-TiO ₂ (1.5%)	-	-	41.67	Natural rubber wastewater	91 (2nd cycle) 42 (3rd cycle)	[7]
PP	UV	DMAEMA	~120 (Oil CA)	Emulsion	~60-70	[35]
PSF	UV	AAc	64.1	Milk water	24-34	[50]

works (Table 4) have all shown that the FRR is high when a membrane surface is modified to be hydrophilic.

SEM photographs of the membranes after protein filtration show more protein molecule fouling on the surface of PSF-O (Fig. 10 (a, e)) than PSF-D (Fig. 10 (b, f)). The surface of PSF-O after NR serum filtration (Fig. 10 (c)) displays heavy organic molecule deposition and the cross-section image of PSF-O (Fig. 10 (g)) shows the presence of organic molecules clogging the pores. The corresponding PSF-D images (Fig. 10 (d, h)) reveal only a modest accumulation of organic molecules on the surface. The PSF-O membrane produced lower FRRs than the PSF-D membrane due to the greater fouling of the membrane and its pores. The SEM observations confirmed the flux and fouling behavior of the membranes indicated by the data in Fig. 7.

Following NR serum filtration, the PSF-D membranes were cleaned, dried in an oven, and again analyzed by FTIR spectroscopy. The results show that the peaks of C=O at 1716 cm^{-1} and -SO_2 at 1125 cm^{-1} were still present but slightly reduced (Fig. 11). Furthermore, the used membrane presented several small new peaks. These new peaks could indicate irreversible fouling, which would correspond with the slightly reduced FRR observed for PSF-D.

The quality of NR serum separation was then evaluated from the rejection of total TSC and total protein of NR serum. The PSF-O membrane rejected 95.9% of total protein and the PSF-D membrane rejected 91.5% (Fig. 12). The rejection of total protein by the modified membrane was 4.4% lower than rejection by the untreated membrane. The rejection of TSC also decreased, from 75.0% for the PSF-O membrane to 72.1% for the PSF-D membrane. The lower rejection of total protein and TSC was possibly due to increased flux [51]. The rejection of total protein was higher than the rejection of TSC because TSC includes all of the solid components in NR serum and covers a wider molecular size distribution than total protein. The greater content of smaller molecules leads to more of them escaping. However, when the higher flux, % FRR, and other properties of the PSF-D membrane are taken into consideration, the PSF-D membrane still performs better than the PSF-O membrane for natural rubber industrial applications.

4. Conclusion

A polysulfone membrane was irradiated with a high-energy electron beam and then reacted with AAC/SSS binary monomers. The highest degree of grafting and surface hydrophilicity was exhibited by a

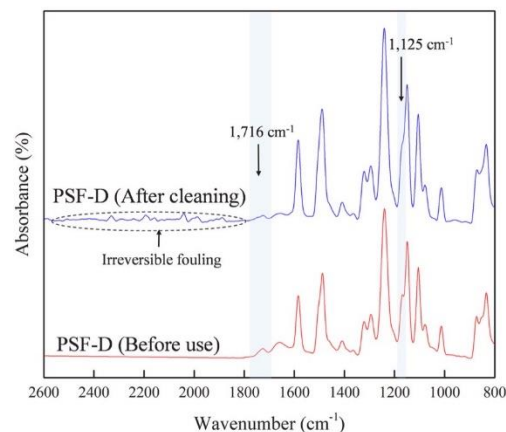


Fig. 11. FTIR spectra of PSF-D membrane before use and when cleaned after use.

membrane that was irradiated with a beam energy of 10 MeV to give an irradiation dose of 50 kGy. This finding was confirmed by analysis of % DOG, water contact angle, surface energy, FTIR spectra, and XPS surveys. Higher electron beam power and radiation dose increased the degree of grafting and hydrophilicity. However, excessive amounts of energy should be avoided. The membrane modified at the higher power and dose performed best overall. Electrostatic interactions at this membrane led to a low flux decay rate, high flux recovery and induced high fluxes of water, BSA protein, and NR serum. In the second of three filtration cycles, the membrane showed a high ratio of flux recovery for BSA and NR serum that confirmed good antifouling properties. When compared to the original untreated membrane, the modified membrane presented a higher level of irreversible resistance toward NR serum filtration. In NR serum filtration, rejections of total solid content and total protein were slightly lower at the modified membrane than at the original membrane. The selected modified membrane showed good antifouling properties toward the natural rubber particles and organic

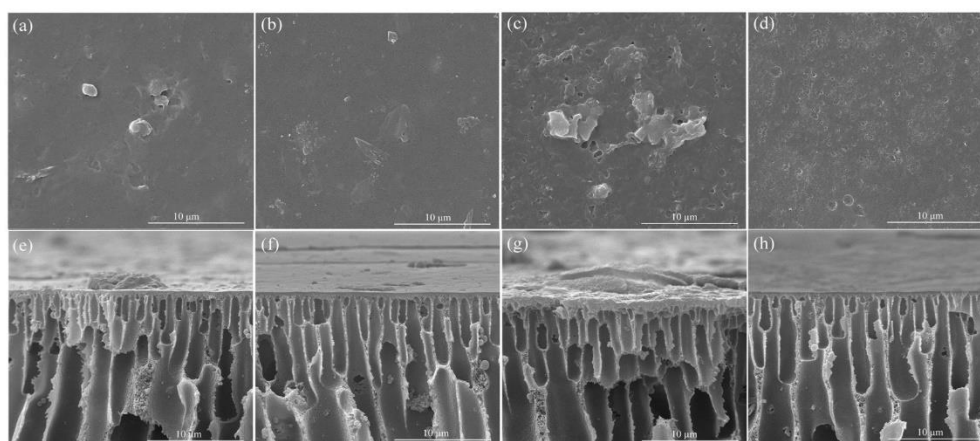


Fig. 10. SEM images show the morphology of the PSF-O membrane after BSA protein filtration (a and e) and NR serum filtration (c and g), and of the PSF-D membrane after protein (b and f) and NR serum (d and h) filtration. All images are at $\times 5000$.

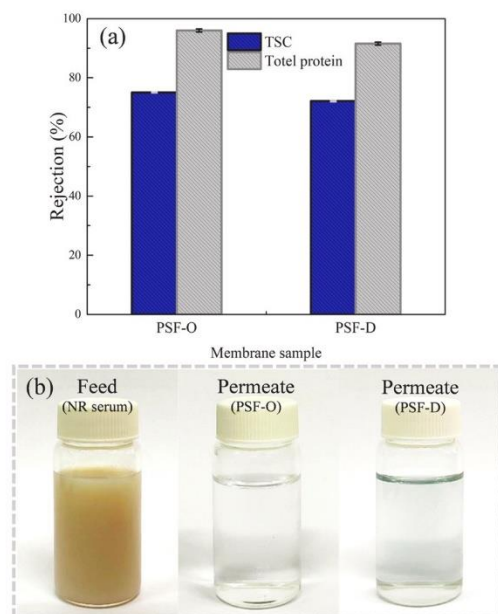


Fig. 12. The rejection of total solid content (TSC) and total protein from NR serum separation (a) and digital photographs of NR serum feed and membrane permeates (b).

molecules found in NR serum. Our research outcome could present a practical solution to the design of membrane surfaces that can be applied to the filtration of natural rubber-based compounds.

CRediT authorship contribution statement

Soraya Ruangdit: Conceptualization, Investigation, Visualization, Writing – original draft preparation. **Thawat Chittrakarn:** Conceptualization, Visualization, Validation, Writing – review & editing. **Chai-porn Kaew-on:** Writing – review & editing. **Ritiron Samran:** Methodology. **Weerapong Bootluckb:** Methodology, Writing – review & editing. **Suksawat Sirijarakul:** Conceptualization, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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CHAPTER 5

CONCLUSION

1. Conclusions

The research was the modification of polysulfone membrane for separation of the components of natural rubber serum (NR serum), natural rubber latex and enhanced filtration properties by the following:

- UV irradiation can be increasing the hydrophilicity of a PSF membrane, which can be following by PEG grafting. The UV radiation has the ability to break down chemical bonds of the PSF polymer membrane, resulting in the formation of polar functional groups on the membrane surface. Varying on UV wavelengths produce different photon energy levels, which influences membrane surface processes and reactions, leading to different surface hydrophilicity responses to treatment time. Furthermore, PEG grafting following UV irradiation was found to extend hydrophilicity for at least 30 days after treatment. Importantly, according to the polar functional groups of PEG on the treated membrane surfaces, the membrane enhanced by the PEG and UV treatment provided good permeability and selectivity at the same time.
- A high-energy electron beam was also used to irradiate a polysulfone membrane, which had been reacted membrane surface and AAc/SSS binary monomers grafting. A membrane that was irradiated with the energy at 10 MeV with a dose of 50 kGy exhibited the maximum degree of grafting (%DOG) and surface hydrophilicity. % DOG, water contact angle, surface energy, FTIR spectra, and XPS surveys all supported this conclusion. Water, BSA protein, and NR serum fluxes have been induced by electrostatic interactions at the membrane surface, which resulted in a low flux decay rate, high flux recovery, and high fluxes of water, BSA protein, and NR serum. The membrane showed a high ratio of flux recovery for BSA and NR serum in the second of three filtration cycles, indicating good antifouling properties. However, total solid content and total protein rejections were slightly lower at the modified membrane than at the original membrane in NR serum filtration. The modified membrane exhibited good anti-fouling characteristics against the natural rubber particles and organic compounds in the NR serum.

Interaction between UV reaction and E-beam has different effects on the polymer membrane surface. The UV irradiation transfer energy to the polymer bonding, and then the surface occurs the active area and grafted with other monomers. However, the UV treatment must use for a long time to treat. The e-beam was momentum transfer

from electron or ion to polymer atom, which created an active area on the polymer membrane surface due to easy grafting of other monomers on the membrane surface. Moreover, the e-beam treatment has a short time to treat and doesn't limit the treated membrane area. Thus, the UV and E-beam treatments have different vantage depending on polymer type, monomer grafting type, application, etc.

In this research, the PSF membrane had better separation performance than the untreated membrane. The modifying PSF with e-beam and AAC/SSS binary monomer showed a good anti-fouling property on the membrane surface. Thus, our results could provide a practical solution for the development of membrane surfaces that can be used for the filtration of natural rubber-based compounds.

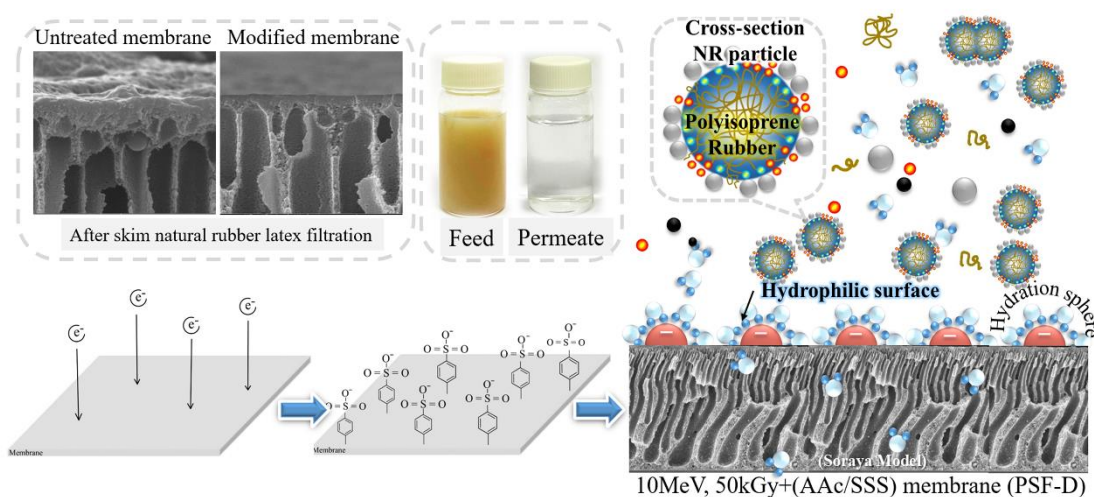


Figure 12 The anti-fouling of modifying membrane.

2. Suggestions

The modification membrane has high anti-fouling properties, but the membrane still has low flux. In the future, we hope to improve our membrane flux to get good for practical use by many techniques such as improving support membrane structure, changing the polymer type of support membrane layer, mixing the hydrophilic additive particles, and so on.

In the future, if the membrane can improve for suitable use in the industries, that can be added-value such as the added value from the range of 4-8% rubber particles recovery from membrane separation techniques. Furthermore, the membrane technique can separate other components such as proteins, carbohydrates, lipids, carotenoids, and inorganic and organic salts from NR serum. These organic molecules from Nature rubber are suitable substrates for the growth of bacterial algae or plankton culture in aquaculture [70]. Some of the research use concentration of the organic molecules in NR serum for fertilizer production. Because all of the products of the concentration

process have economic value, this method might reach "zero discharge." [5]. Although no exact valuation is currently available, this research is expected to be a starting point for future improvements in membranes for NR serum separation.

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List of Publication and Proceeding

- S. Ruangdit, T. Chittrakarn, C. Kaew-on, R. Samran, W. Bootluck and S. Sirijarukul, (2022), E-beam induced grafting of binary monomer on polysulfone membrane for the separation of skim natural rubber latex, Journal of Environmental Chemical Engineering, S2213-3437 (22) 00735-7, <https://doi.org/10.1016/j.jece.2022.107862>.
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International Conference

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