POLYVINYL ALCOHOL-CROSSLINKED POLYVINYLIDENE FLUORIDE HOLLOW FIBER MEMBRANE FOR CRUDE PALM OIL REFINING

RABIAH ASSYAMIYAH BINTI AZMI

UNIVERSITI TEKNOLOGI MALAYSIA

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RABIAH ASSYAMIYAH BINTI AZMI

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For my beloved mother and father,

my husband and daughter,

my brothers and sisters,

colleagues, and friends.

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ABSTRACT

Over recent years, there has been an explosive growth of interest in the development of alternative approaches for crude palm oil (CPO) refining. During a typical refinery process, free fatty acid (FFA) is one of the key impurities that need to be reduced if not completely removed from CPO in order to minimize their detrimental effects on the oil quality. Polyvinylidene fluoride (PVDF) membrane shows great potential in removing FFA from CPO owing to its hydrophobic properties, high mechanical strength and good thermal stability. However, low concentration of FFA in CPO, which is normally ranging from 3 to 5%, has hindered the capability of the membranes to separate the trace amount of FFA from the bulk. Thus, modification of PVDF membrane is essential to enhance the interaction between the membrane surface and FFA molecules to facilitate efficient FFA removal. In order to achieve this purpose in the present study, the outer surface of PVDF hollow fiber membranes was crosslinked with polyvinyl alcohol (PVA). Glutaraldehyde was used as a crosslinking agent to avoid the PVA dissolution. Morphological change was observed on the membrane surface with longer immersion time during the crosslinking process. The contact angle was significantly reduced in proportional to the concentration of PVA used for the crosslinking, addition of catalyst which is hydrochloric acid as well as the immersion time, which indicates the enhanced surface hydrophilicity. Additionally, the average roughness of the crosslinked PVDF membranes increased with the increasing of PVA concentration. The results obtained showed that the PVDF hollow fiber crosslinked with 100 ppm PVA exhibited the highest FFA rejection of 5.93% after 3 hours of operation. In addition, the membrane also capable of removing phosphorus content as high as 90% rejection as well as partial reduction of its colour intensity. This study served as the first attempt of CPO deacidification through membrane system without the addition of any chemical during the filtration process.

ABSTRAK

Kebelakangan ini, terdapat tarikan dalam pembangunan pendekatan alternatif untuk penapisan minyak sawit mentah (CPO). Semasa proses penapisan biasa, asid lemak bebas (FFA) adalah salah satu daripada bendasing yang perlu dikurangkan jika tidak dinyahkan sepenuhnya daripada CPO untuk mengurangkan kesan yang memudaratkan kualiti minyak. Membran polivinilidina florida (PVDF) menunjukkan potensi yang besar dalam menyingkirkan FFA daripada CPO kerana sifat hidrofobik, kekuatan mekanikal yang tinggi dan kestabilan haba yang baik. Walau bagaimanapun, kepekatan FFA yang rendah dalam CPO, biasanya antara 3 hingga 5%, telah menghalang keupayaan membran untuk memisahkan sejumlah kecil FFA ini daripada CPO. Oleh itu, pengubahsuaian membran PVDF adalah penting untuk meningkatkan interaksi antara permukaan membran dan molekul FFA, bagi memudahkan penyingkiran FFA. Untuk mencapai tujuan ini, dalam kajian ini, permukaan luar membran gentian geronggang PVDF telah ditaut silangkan dengan polivinil alkohol (PVA). Glutaraldehida telah digunakan sebagai agen taut silang untuk mengelakkan PVA daripada terlarut. Perubahan morfologi dapat dilihat pada permukaan membran dengan masa rendaman yang panjang semasa proses taut silang. Sudut sentuhan berkurangan dengan ketara dengan penambahan kepekatan PVA yang digunakan untuk proses taut silang, penambahan pemangkin iaitu asid hidroklorik serta masa perendaman, menunjukkan permukaan hidrofilik dipertingkatkan. Selain itu, purata kekasaran permukaan membran PVDF yang ditaut silang meningkat dengan kepekatan PVA. Keputusan yang diperoleh menunjukkan gentian geronggang PVDF yang ditaut silangkan dengan 100 ppm PVA mempamerkan penyingkiran FFA yang paling tinggi iaitu 5.93% selepas 3 jam beroperasi. Di samping itu, membran juga mampu mencapai peratus penyingkiran fosforus sebanyak 90% serta pengurangan separa keamatan warnanya. Kajian ini merupakan percubaan pertama penyahasidan CPO menggunakan sistem membran tanpa penambahan sebarang bahan kimia semasa proses penapisan.

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LIST OF ABBREVIATIONS

AFM	-	Atomic force microscopy
AOCS	-	American Oil Chemists' Society
$CaCl_2$	-	Calcium chloride
CPO	-	Crude palm oil
DG	-	Diglycerol
DOPA	-	3,4-dihydroxyphenylalanine
EDTA	-	Ethylene diamine tetracetic acid
EG	-	Ethylene glycol
FESEM	-	Field emission scanning electron microscopy
FFA	-	Free fatty acid
FTIR	-	Fourier transform infrared spectroscopy
GA	-	Glutaraldehyde
HCl	-	Hydrochloric acid
HF	-	Hydrogen fluoride
MEUF	-	Micelle enhanced ultrafiltration
MD	-	Membrane distillation
MF	-	Microfiltration
MG	-	Monoglycerol
MWCO	-	Molecular weight cut-off
NaCl	-	Sodium chloride
NaOH	-	Sodium hydroxide
NF	-	Nanofiltration
NMP	-	N-methyl-2-pyrrolidone
PA	-	Phosphatic acid
PC	-	Phosphatidyl choline
PE	-	Phosphatidyl ethanolamine
PEG	-	Polyethylene glycol

PI	-	Phosphatidyl inositol
PL	-	Phospholipid
PV	-	Pervaporation
PVA	-	Polyvinyl alcohol
PVDF	-	Polyvinylidene fluoride
PVP	-	Polyvinylpyrrolidone
RO	-	Reverse osmosis
SDS	-	Sodium dodecyl sulfate
SEM	-	Scanning electron microscopy
TGA	-	Thermal gravimetric analysis
TG	-	Triglyceride
UF	-	Ultrafiltration
UV	-	Ultraviolet

LIST OF SYMBOLS

A	-	Effective membrane area
C_p	-	Content in permeate
C_f	-	Content in feed
J	-	Flux
Q	-	Quantity of permeate
t	-	Time
R	-	Rejection
R_a	-	Mean roughness
R_{max}	-	Maximum roughness
R_{ms}	-	Root mean square of Z values

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Palm oil production is vital for the economy of Malaysia where the oil palms yield an average of 3.7 tonnes of oil per hectare per year in Malaysia, making Malaysia as one of the biggest producers of palm oil (Idrees, 2014). In palm oil industry, refining process in general involves removal of undesirable constituents such as free fatty acids (FFA), phospholipid (PL), colour pigment and trace metals from crude palm oil (CPO), making the refined oil meeting the acceptable effects. Other impurities of nutritional values include tocopherol, tocotrienol and carotene. However, tocopherol and tocotrienol act as natural antioxidants that protect the oil from oxidation and as vitamin E, while α- and β-carotene are precursors of vitamin A.

In the past years, CPO was refined using either chemical or physical methods. Both of these methods involve the addition of chemicals which are phosphoric acid as well as bleaching earth in degumming and bleaching process respectively. During degumming process, amount of phosphoric acid used must be controlled properly since it can lead to the darkening and instability of the oil if the excess was not removed properly (Thiagarajan and Tang, 1991). Meanwhile, treatment of oil with sodium hydroxide in chemical refining, results in oil loss attributed to emulsification, and oil occlusion in soapstock and saponification (Young, 1981). Besides, large amount of water is needed in the conventional techniques which in the end will generate large amount of wastewater from the plant. These disadvantages of conventional method have led to an interest of developing a new approach in CPO refining. Membrane separation on the other hand offers an alternative with high efficiency for CPO refining since it can be operated at ambient temperature, does not require phase change, can simultaneously concentrate, fractionate and purify products (Dziezak, 1990).

Membrane separation shows great potential in CPO refining since membrane can be used in almost all stages of oil production and purification (Raman *et al.*, 1996). However, in terms of CPO deacidification through FFA removal, low concentration of FFA in CPO has reduced the capability of membrane to separate the trace amount of FFA from the bulk. In order to establish an effective separation process, it is important to develop highly selective membranes where it will provide affinity interactions difference between various permeating constituents with the membranes (Xu *et al.*, 2005). Hence, modification of membrane surface to improve the affinity between the membrane surface and FFA molecule seems to be a promising solution.

Several modifications on membrane surface have been used to improve the membrane performance. Physical modification includes blending and surface coating with the desired polymer while chemical modification includes copolymerization, grafting, and plasma treatment. Surface coating is a convenient and practical method because it can modify the membrane surface properties while retaining the stability of the bulk polymer (Du *et al.*, 2009). However, chemical treatments such as sulfonation and crosslinking on the membrane surface are necessary to anchor the coated layer (Liu *et al.*, 2011).

Since FFA, which is a carboxyl derivative and hydroxyl material, may show high affinity selectivity for FFA because of the interaction between the hydroxyl material and carboxyl group of FFA, PVA with -OH functional group can be used to increase the affinity of FFA towards membrane. Modification of PVDF with PVA has been practiced by several methods which include blending (Li *et al.*, 2010), surface coating by solid-vapor interfacial crosslinking (Du *et al.*, 2009) and PVA grafting by immersion (Mansouri and Fane, 1999). PVA grafting by dipping the membrane into PVA solution that has been crosslinked is by far the most simple and convenient way.

To avoid its dissolution during deacidification process, the PVA coating layer is crosslinked. Several types of crosslinkers have been explored to have potential as an effective crosslinking agent. Covalent crosslinking of PVA with aldehyde is widely practiced (Barbari and Li, 1995; Bolto *et al.*, 2009; Dai and Barbari, 2000; Djennad *et al.*, 2003; Plieva *et al.*, 2006; Wang *et al.*, 2006). Among all the aldehyde crosslinker, glutaraldehyde is a more effective than formaldehyde or glycidyl acrylate which produce a less swollen product (Bolto *et al.*, 2009). It can react with different PVA chains yielding intermolecular crosslinking and intra-polymer network (see Figure 1.1). Acid catalyst is sometimes used to enhance the reaction during the crosslinking process.

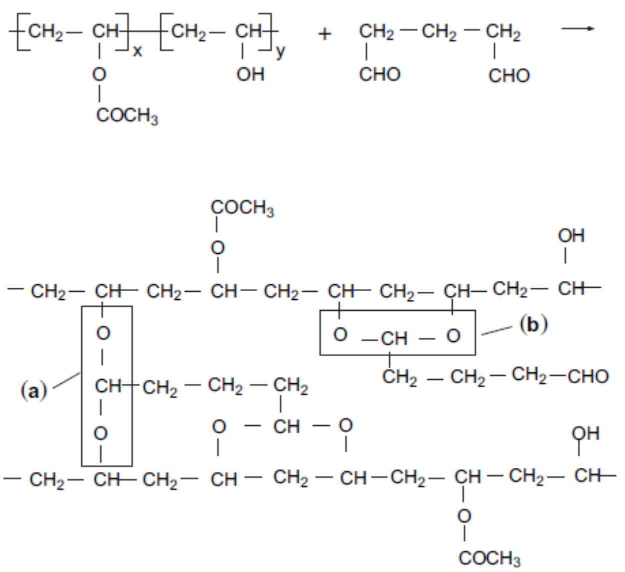

Figure 1.1: Structure of crosslinked PVA: (a) intermolecular crosslinking and (b) intramolecular crosslinking (Du *et al.*, 2009)

In modifying a membrane, modification parameters have significant effects on the characteristics of the active layer, and therefore on the performance of modified membrane (Du *et al.*, 2009). High molecular weight PVA results in a more densely packed spiral configuration than low molecular weight PVA thus increasing the resistance. In order to avoid a dense PVA layer, a thin coating layer is sufficient enough to attract the FFA. Hence, PVA concentration should be low but sufficient to optimize the attraction of FFA. The crosslinking time should be long enough to obtain adequate coverage through adsorption, but also as short as possible to prevent pore blockage. Crosslinking time also determines the density of the crosslinking network, which should be short to favor permeation during deacidification process but long enough to prevent PVA dissolution. Hence, all the parameters need to be optimized to obtain an effective PVDF-PVA membrane.

In this study, several parameters were manipulated in order to achieve an optimum modified membrane for CPO refining. PVA concentration, immersion time, as well as addition of catalyst were manipulated and several characterizations were performed on the membrane to identify the effects of those variations on the membrane properties as well as performance. The resultant membrane was expected to result in the successful production of a high quality refined palm oil.

1.2 Problem Statement

Industrially, refining process (chemical and physical refining) has several drawbacks which are loss of oil and nutrients, high energy consumption, huge usage of water and chemicals and all of these lead to loss in overall profit. The deacidification has the maximum economic impact on oil production. Any inefficiency in this process has a great bearing on the subsequent process operations. The removal of FFA from CPO represents the most delicate and difficult stage in refining cycle, since it determines the quality of the final product.

During the chemical deacidification process, there are always considerable losses of neutral oils, sterol, tocopherols and vitamins. The disposal and utilization of resulting soapstock may also create problems of environmental pollution. Meanwhile in physical deacidification, practical results have shown that it leads to acceptable results only when good quality starting oils are used. The incomplete removal of undesirable components during the pretreatment of oil has to be compensated for by an increased used of bleaching earth. These conclude that there are several drawbacks to today's technology, and so alternative approaches are needed to overcome these drawbacks.

One of the new approaches to overcome the major drawbacks of conventional processes is membrane-based refining process. The feasibility of using membrane technology in oil industry has been widely reported in the literature (Alicieo *et al.,* 2002; Arora *et al.,* 2006; de Morais Coutinho *et al.,* 2009; Hafidi *et al.,* 2005; Manjula *et al.,* 2011; Ochoa *et al.,* 2001; Pagliero *et al.,* 2007; Pioch and Largue, 1998; Raman *et al.,* 1996). Membrane-based technology can be favorably operated at ambient temperature without undergoing phase changes. This technology can also be used to simultaneously concentrate, fractionate and purify products (Hwang, 2010; Raman *et al.,* 1996). Owing to its versatility, membrane technology can be applied in almost all the stages of oil processing (Kale *et al.,* 1999). The main advantages of using membranes in edible oil industry are low energy consumption, preservation of desirable components in the oil and elimination of wastewater treatment. In the technological and nutritional point of view, reduction of energy cost as well as the retention of nutrients are highly desired in the oil processing industry (Cui and Muralidhara, 2010). Most importantly, membrane technology offers an attractive refining route where the usage of chemicals such as sodium hydroxide can be avoided throughout the process.

Despite the considerable research efforts pursued in the last few decades, only a few commercial applications of membrane technology for edible oil processing have been reported. Various attempts made on the deacidification and degumming of edible oils using membrane technology are summarized in Table 1.1. Undeniably, despite showing potential in removing the undesired phosphatides content from the vegetable oil, membrane separation was insufficient to effectively remove FFA from the edible oil. In fact, it has been generally presumed that addition of alkali is essential to completely deacidify the oil (Bhosle and Subramanian, 2005). The limitation encountered in this aspect has stumbled the further development of membrane technology in edible refining process.

Table 1.1: Membrane technology applications for edible oil refining process.

Polymer	Vegetable Oil	Achievements	Drawbacks	Reference
PSU	Soybean Oil	R = 34.39%	Soap	Alicieo *et al.*, 2002
Cellulose	Sunflower oil and Rapeseed Oil	Results varied depending on the concentration of solvent of additive used.	-Chemicals are needed to produce oil permeate of high quality -Fouling	Pioch *et. al.*, 1998
PA	Model fatty acid solution	R=75-84%	-Methanol is required to extract FFA. -Low solvent stability of membrane against alcohol.	Raman *et. al.*, 1996

*R=Rejection of FFA

Although membranes have been commonly known for their separation principle which based on size exclusion mechanism, the understandably ineffectiveness of membrane separation for deacidification of CPO is primarily ascribed to the small molecular weight difference between the triglycerides (oil molecules) and FFAs, which has in turn upset the capability of membrane separation. To further complicate the issue, the low concentration of FFA in CPO, which is normally in the range of 3 to 5%, is also found to hamper the capability of membrane to separate the trace amount of FFA from the bulk. In order to combat the identified shadow side, membranes with precise selectivity towards FFA are highly desired to perform the deacidification process. In this context, it is important to develop highly selective membranes to render strong interactions between the membrane surface and FFA molecules.

In this study, PVDF membranes have been crosslinked with PVA in order to improve the interaction between FFA and membrane. Since PVDF membrane has been extensively applied in many separation processes, and serves as a potential candidate in CPO refining, it is important to apply a mild modification on PVDF membrane to retain the desired separation properties while optimizing the crosslinking condition in removing FFA from CPO.

1.3 Research Objectives

The objectives of this research are as follows:

a) To fabricate and characterize crosslinked PVDF hollow fiber membranes for CPO refinery.
b) To evaluate the performance of crosslinked PVDF for CPO refining
c) To optimize the condition of crosslinking that affects the performance of the membrane.

1.4 Research Scopes

In order to achieve the objectives, the following scopes are identified:

a) Fabricating 18 wt% PVDF hollow fibres for degumming and deacidification processes.
b) Producing degummed oil by reducing the phosphorus content of the CPO using the neat PVDF hollow fiber membrane.
c) Performing a crosslinking process of PVDF with PVA by using glutaraldehyde as the crosslinking agent.
d) Performing membrane characterization using scanning electron microscope, field emission scanning electron microscope, thermal gravimetry analysis, fourier transform infrared spectroscopy, atomic force microscope, solute rejection test, and contact angle.
e) Conducting the degumming and deacidification process by using a pressure driven filtration system.
f) Manipulating the PVA concentration (100-5000 ppm), addition of catalyst (HCl), immersion time of crosslinking (0.5-48 hours) and PVA:GA ratio to optimize the membrane crosslinking.
g) Performing analysis on the oil samples in term of rejection in colour, phospholipid and FFA content.

1.5 Significance of Study

The main contribution and novelty of this research is the design and development of a new membrane-based system for simultaneous degumming and deacidification of CPO for the production of high quality oil. This study served as an attempt of CPO refining using pressure-driven membrane system without the addition of any chemical in the CPO. Up to date, no similar effort has been reported for the deacidification of CPO. In fact, it has been generally presumed that addition of alkali is essential to successfully deacidify the oil (Bhosle and Subramanian, 2005).

Absence of sodium hydroxide (NaOH) usage in deacidification process and phosphoric acid in degumming process will give many advantages in terms of cost-reduction which will result in the increase of overall profit. Addition of NaOH and phosphoric acid in the CPO through chemical refining in industry can lead to the instability of the oil as well as resulting in oil loss due to saponification. Meanwhile, membrane separation offers an alternative cost effective and efficient method for CPO refining since it requires low energy consumption, preservation of desirable components in the oil and elimination of wastewater treatment.

In this study, the feasibility of crosslinked PVDF membrane for refining of CPO has been investigated. The findings of this work showed that the membrane-based CPO refining has a potential to eliminate not only FFA but also phospholipids without addition of any chemical throughout the process. As the conclusion, the outcome of this project has resulted in a minimum development of cost effective and energy efficient membrane-based system that provides great economic with little adverse environment impacts.

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