EFFECT OF PHYSICAL AND MECHANICAL PROPERTIES OF PU BIOPOLYMER MEMBRANES UPON USE OF DIFFERENT FABRICATION TECHNIQUES

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Especially dedicated to my loving mum Pn Arbi Binti Kasim, my dearest siblings Rahimy, Rahida, Parhani, and best-est friend ever Noor Syafiqa..thanks for your prayer and nonstop support given to me to complete this research..may ALLAH grace and bounty be upon them

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With the name of Allah, the Almighty.

"Indeed, in the creation of the heavens and the earth and the alteration of the night and the day are signs for those of understanding. Who remember Allah while standing or sitting or (lying) on their side and give thought to the creation of the heavens and earth, (saying), "Our Lord, You did not create this aimlessly; exalted are You (above such a thing); then protect us from the punishment of the Fire".
(Al-Imran: 190-191)
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Abstract

In developing polymer membranes that response to prevents liquid water from penetrating through, while at the same time permitting moisture past out through, polymer membrane with various structure ranging from dense to highly asymmetric morphologies (0.01 - 0.25 mm) were fabricated through three different techniques; blends, curing and grafting fabrication. From FT-IR analysis, BP/PEG (blends, curing and grafting) were fully converted into solid polymer membrane with functional group of N-H stretching in region 3350 - 3250 $cm^{-1.}$ Morphological result of BP/PEG shows three types of surface; open, close and blind surface with cylindrical blind and ink bottle shaped structure randomly. Due to lower porosity of skin over a symmetric support acts as a barrier, BP/PEG polymer membranes resultant no water permeability as compared to BP/DMF, which exhibit extremely higher water permeability with value 0.161 $L/s.m^3$ at lower concentration. Water absorption analysis shows that mechanical properties of the prepared membranes were significantly influenced by their structure and amount of water absorbed. Thus, BP/PEG (blends, curing and grafting) preparation gave lower amount of water absorption with less than 0.01% water absorption increment rather than BP/DMF 12% (w/v) with highly porosity value of 0.07%. Thermogravimetric analysis (TGA) reviewed that the hard segment decomposition temperature was occur at 295 ^{0}C – 395 ^{0}C, meanwhile for soft segment at 370 ^{0}C – 500 ^{0}C. Based upon modulus, tensile, strain and tear strength also energy at break, evidently shows that the BP/PEG (grafting) method gave the best performance on physical and mechanical properties with highest mean value of 12419 N/mm, 14.11 MPa, 38.289 %, 50.67 N/mm and 21.627 N respectively. Reciprocally, PEG solvent does significantly increase the mechanical properties with the reaction of BP rather than DMF solvent with varieties of concentration. Moreover, BP/PEG membrane from each fabrication technique had obvious dense porous structural feature with open, close and blind pores in practically boundless development as of adequate final use in membrane application.

Abstrak

Dalam membangunkan polimer membran yang menghalang tindak balas cecair daripada meresap dan pada masa yang sama membenarkan kelembapan melaluinya, polimer membran dengan pelbagai struktur, terdiri daripada morfologi yang padat sehingga simetri yang tertinggi (0.01 - 0.25 mm) telah dihasilkan melalui tiga teknik berbeza; campuran *(blends)*, ikatan *(curing)* dan cantuman (*grafting*). Daripada analisis FT-IR, BP/PEG (campuran ,ikatan dan cantuman) telah ditukar sepenuhnya kepada polimer membran dengan kumpulan berfungsi NH regangan dalam rantau 3350-3250 cm^{-1}. Hasil morfologi, BP/PEG menunjukkan tiga jenis permukaan; terbuka, rapat dan buta dengan struktur silinder buta dan botol dakwat. Disebabkan oleh keliangan permukaan, sokongan simetri bertindak sebagai penghalang, BP/PEG polimer membran yang dihasilkan, tidak kebolehtelapan air berbanding BP/DMF, yang mempamerkan kebolehtelapan air yang sangat tinggi dengan nilai 0.161 L/s.m3 pada kepekatan yang lebih rendah. Analisis penyerapan air menunjukkan, sifat-sifat mekanikal membran ketara dipengaruhi oleh struktur dan jumlah air yang menyerap. Oleh itu, BP/PEG (campuran, ikatan dan cantuman) memberikan jumlah yang lebih rendah iaitu kurang 0.01 % air kenaikan penyerapan, berbanding BP/DMF 12% (w/v) dengan keliangan tertinggi iaitu 0.07 %. Termogravimetri analisis (TGA) mengkaji bahawa segmen keras suhu penguraian berlaku pada 295 ^{0}C - 395 ^{0}C , sementara bagi segmen lembut pada 370 ^{0}C - 500 ^{0}C. Berdasarkan modulus, tegangan, tekanan dan kekuatan tenaga berhenti, jelas menunjukkan bahawa kaedah BP/PEG (cantuman) menunjukkan persediaan yang terbaik pada sifat-sifat fizikal dan mekanikal dengan nilai min tertinggi 12419 N / mm, 14.11 MPa, 38,289 %, 50.67 N /mm dan 21,627 N setiapnya. Pelarut PEG ketara meningkatkan sifat mekanik dengan tindakbalas BP berbanding pelarut DMF. Selain itu, BP/PEG membran dari setiap teknik fabrikasi mempunyai ciri-ciri yang struktur jelas tebal berliang dengan liang terbuka, berhampiran dan buta dalam pembangunan praktikal terbatas pada penggunaan akhir yang mencukupi dalam aplikasi membran.

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LIST OF SYMBOLS

MDI	:	4,4'-Methylen-bis-(phenylisocynate)
PEG	:	Polyethylene glycol
HDMI	:	Hexamethylene Diisocyanate
DMF	:	N,N-dimethylformamide
SEM	:	Scanning Electron Microscope
UTM	:	Universal Testing Machine
FTIR	:	Fourier Transform Infrared
TGA	:	Thermogravimetric
PU	:	Polyurethane
ºC	:	Degree Celcius

CHAPTER 1

INTRODUCTION

1.1 Background of Research

Membrane and membrane processes are not a recent invention and it is a part of our daily life. Membrane technology is now been industrially establish in impressively large scale after a long period through the producing of biological membrane. As reported [1], the key property is the ability of membranes to control the permeation rate of water and liquid through the membranes. According to Baker *et al.* [2], polymeric membranes have reached high growth and have gained an important place in broad range of applications including in industrial sectors, gas separation, wastewater treatment, food processing, medical devices and many others.

Due to the concern about global warming and the contribution of greenhouse effect has increased dramatically; the use of renewable resource in the preparation of various applications has been revitalized as studied [3]. Walpoth *et al.* [4] had been studied that vegetable oil is one of the most valuable to develop as raw materials for membrane. As reported [4], vegetable oil offer advantages such as low cost, acceptable specific properties, biodegradability and availability of renewable resources.

Medical devices are one of membrane applications which are fast growing field that represents the largest consumption of membrane area per year as reported [5]. In terms of total membrane produced, medical applications are at least equivalent to all industrial membrane applications. By focusing to a very high cost of getting medical devices in particular of dental bib for dental clinic use, proposed an ideas to developing polymer membrane that respond to moisture/liquid content for use as a protective clothing based on renewable resources (vegetable oil).

AnikaZafiah in her studied [6-7], plant oils and their derivatives have been used by polymer chemists due to their renewable nature, world wide availability, relatively low price, and their rich application possibilities, in which its main constituent are triacylglycerols. Several arguments can be found to believe in the great potential of plant oils as an alternative resource for the production of polymeric materials as reported [7].

In the context of renewable, plant oils offer many advantages apart from its renewability. Their world-wide availability and relatively low prices make them industrially attractive and feasible, as daily demonstrated with industrial oleochemistry. Furthermore, diverse chemistry can be applied on them, leading to a large variety of monomers and polymers [8].

1.2 Problem Statement

Although, there are many techniques that have been used in polymer membrane application, however it were not meet all the performance requirements for a membrane dedicated to a particular application.

According to Sin *et al.* [9] through solvent casting techniques, it may yield the following disadvantages such as skin of nonporous polymer of the surface, non-homogeneous dispersion of pores, lack of inner connectivity of the pores and remaining porogen within the scaffold after porogen leaching.

Other than that, through gas foaming, this technique resulting many pores are closed with lack of pore inner connectivity as reported by Strathman *et al.* [10] . Therefore membrane modifications are gaining rapidly increasing importance such as blending, curing and grafting.

The volume of petroleum-based synthetic material such as plastic, appear as wastes presents disposal authorities with an increasingly very serious problem and becoming implication to the environmental problem as reported by Huayu *et al.* [11]. At one time it was relatively inexpensive to dispose of domestic and industrial waste in holes in the ground.

Lucas *et al.* [12] in studied, reported that plant oils and their derivatives have been used by polymer chemists due to their renewable nature, world wide availability, relatively low price, and their rich application possibilities. Furthermore, Nayak *et al.* [13] studied that by increasing demand of industrial raw materials to use the renewable resources, vegetable oils were brought focus as a potential source of raw materials. This is due to their potential to substitute petrochemical derivatives as studied [13].

According to Gogolewski *et al.* [14], even polymeric membranes dominating a very broad range due to its advantages, however membrane polymer also have their limitations. This include, a very well-defined regular pore structure is difficult to achieve. In addition, mechanical strength, thermal stability and the chemical resistance are rather low for many organic polymers.

In contrast, some inorganic materials have disadvantages such as very brittle, and due to complicated preparation methods and manufacturing technology, the prices for many inorganic membranes are still very high.

1.3 Aim of Research

The key aim of this research is to early develop renewable biopolymer membranes based on new functional group by means of FTIR, morphological structure by SEM, water permeability, thermal stability by TGA, and mechanical properties (tensile and tear strength) through the different membrane preparation technique (curing, blends and grafting technique) with correlation of their membrane structure and property.

1.4 Scope of Research

This research focuses on developing renewable biopolymer membranes which based on three different membrane preparation technique; curing, blends and grafting. Polymer membranes with different range of pore (1 -100 µm) and thickness (0.01 - 0.25 mm) were prepared.

Chemical composition of the functional group was studied by using Fourier Transform Infrared Spectroscopy (FTIR) while Scanning Electron Machine (SEM) is to investigate the influences of the fabrication technique on membranes surface morphological structure. Studies of thermal stability and mechanical properties were observed by using Thermal gravimetric analysis (TGA), tensile and tear strength by Universal Testing Machine (UTM) respectively. In addition, permeability was determined by using water permeability, water absorption/water uptake analysis to measure the amount of water through the pore of membranes.

1.5 Objectives of Research

i. To fabricate renewable polymer membrane via three different technique preparation: BP/PEG (blends) - 1ply, BP/PEG (curing) – 2 plies and BP/PEG (grafting) – 1 ply with PEG.

ii. To determine the best fabrication techniques based on the physical and mechanical property functional group determination via FT-IR.

iii. To investigate the morphology, decomposition, water permeability, water absorption and mechanical properties, physical and structure of polymer membranes via Scanning Electron Machine (SEM), Thermogravimetric Analysis (TGA), water permeation and Universal Testing Machine (UTM).

CHAPTER 2

LITERATURE REVIEW

2.1 Background of Membranes

A membrane is an interphase between two adjacent phases acting as a selective barrier, regulating the transport of substances between the two components as studied by Klempner *et al*. [15]. In general, membranes are thin layers, that can have significantly different structures, but all have the common feature of selective transport to different components in a feed. Mulder *et al*. [16] from his studied, state that membranes are generally classified by the nature of the materials, selective barrier, structure, membrane morphology, geometry, preparation method, separation regime and process.

Membranes and membrane processes were first introduced as an analytical tool in chemical and biomedical laboratories and then developed very rapidly into industrial products with significant technical and commercial impact as reported [16]. According to Gogolewski *et al*. [17], membranes are used on a large scale in wide range of application areas such as to produce potable water from sea and brackish water, to clean industrial effluents and recover valuable constituents, to concentrate, purify, or fractionate macromolecular mixtures in the food and drug industries, and to separate gases and vapors in petrochemical processes. It also plays as key components in energy conversion and storage systems, in chemical reactors, in artificial organs, and in drug delivery devices.

Lonsdale [18] in his studied, explain that membranes used in the various applications differ widely in their structure, function and the way operated. However, all membranes have several features in common that make them particularly attractive tools for separation of molecular mixtures. Most important is that the separation is performed by physical means at ambient temperature without chemically altering the constituents of a mixture.

According to Drioli *et al*. [19], although synthetic membranes are widely used as valuable scientific and technical tools in a modern industrialized society, they are not very well defined in terms of their structure and function. The most prominent association that many people have when thinking of a membrane resembles that of a filter. However, a membrane can be much more complex in both structure and function.

Bhattacharyya *et al.* [20] has summarized, the permeability of a membrane is a measure of the rate at which a given component is transported through the membrane under specific conditions of concentration, temperature, pressure, or electric field. The study [21] shows, the transport rate of a component through membrane is determined by the structure of the membrane, by a size of permeating component, by the chemical nature and the electrical charge of the membrane material and permeating components, and by the driving force such as concentration, pressure or electrical potential gradient across the membrane.

Drioli *et al.* [22] studied, the use of different membrane structures and driving forces has resulted in a number of rather different membrane processes such as reverse osmosis, microfiltration, ultrafiltration, nanofiltration, dialysis, electridialysis, Donnan dialysis, pervaporation, gas separation, membrane contactors, membrane distillation, membrane based solvent extraction, membrane reactors and others.

2.2 Membranes Classification

Membranes are grouped into polymeric and inorganic membranes. Membranes may be homogeneous or heterogeneous, symmetrical or asymmetrical, and porous or non-porous or with special chemical affinity dictated the mechanism of permeation and separation. They also can be organic or inorganic, liquid or solid. The permeation properties of polymer membranes are strongly influenced by both the preparative route used and the final configuration (isotropic, asymmetric or composite) of the membrane by studied [23]. The membrane classifications are shown in Figure 2.1.

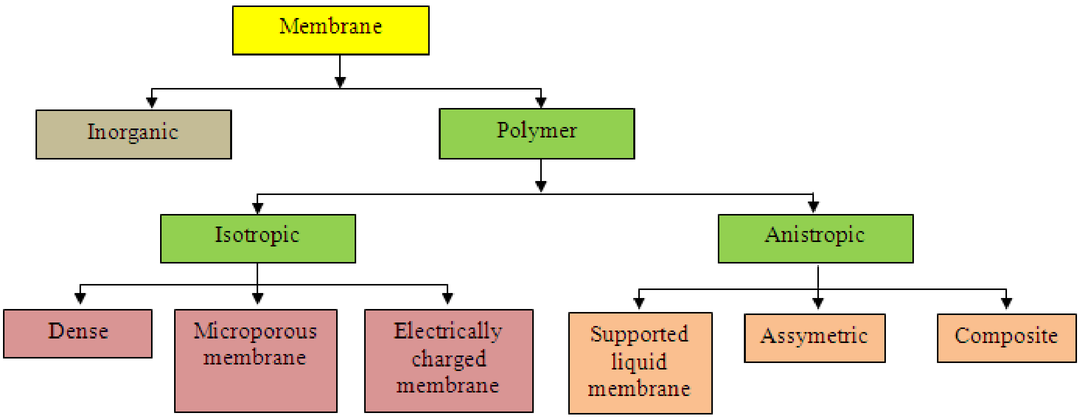


Figure 2.1: Membrane classification [22]

From Zhang *et al.* [24] studied that in essence, a membrane is nothing more than a discrete, thin interface that moderates the permeation of chemical species in contact with it. This interface may be molecularly homogeneous, that is, completely uniform in composition and structure, or it may be chemically or physically heterogeneous. Figure 2.2 shows the schematic diagrams of the principal types of membranes.

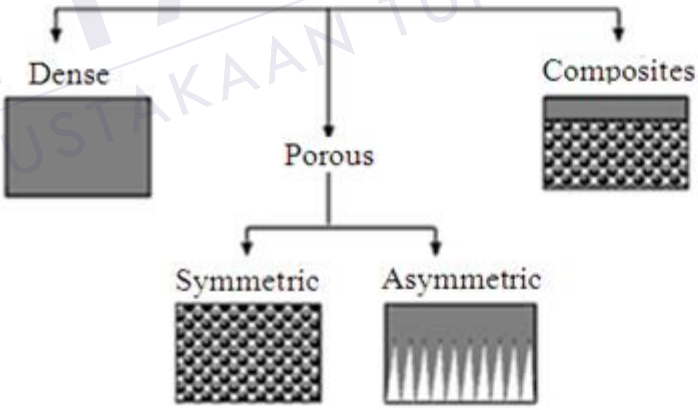


Figure 2.2: Membrane classification according to the morphology [24]

2.2.1 Isotropic Membranes

Isotropic microporous membranes have a rigid, interconnected pore, voided and structure distributed randomly. The separation process is controlled by the pore size distribution of microporous membranes and the hydrodynamic conditions. The microporous membranes are prepared by phase separation, tracked etch, stretching, or leaching. The phase separation is the most important method for the isotropic microporous membrane preparation[25]. Figure 2.3 shows the schematic diagram of different membrane morphologies.

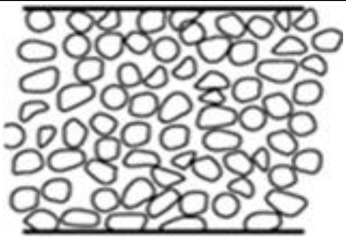
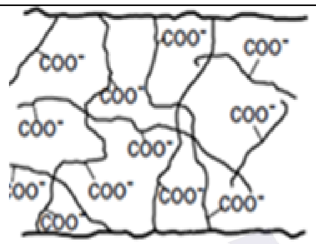
(a) Dense membrane	(b) Microporous membrane	(c) Electrically charged membrane
		

Figure 2.3: Schematic diagram of different membrane morphologies of isotropic membrane [25]

As refer to Figure 2.3(a) of dense membrane morphology, studies from Krause *et.al* [26] shows that dense membranes, also called “diffusion” membranes have no open pores in the membrane wall or the outer skin of the wall. This membrane is rarely used in practical membrane separation process because of its low flux caused by its high membrane thickness, but the intrinsic properties of polymers will determine the membrane performance and separation characteristics. Likewise, Marcano *et al.* [27], explain that dense membranes are mainly used in laboratory to characterize the intrinsic membrane properties for control release, gas separation, pervaporation, nanofiltration, and reverse osmosis membranes for material screening. They are prepared by solution casting and thermal melting extrusion approaches.

According to Klaaseen *et al.* [28], dense membranes consist of a dense film through which permeate are transported by diffusion under the driving force of a pressure, concentration, or electrical potential gradient. The separation of various components of a mixture is related directly to their relative transport rate within the membrane, which is determined by their diffusivity and solubility in the membrane material. Thus, nonporous, dense membranes can be separate permeants of similar size if their concentration in the membranes to perform the separation. Usually these membranes have an anisotropic structure to improve flux. However, the advantage of these membranes was their relatively high wall thickness due to mechanical requirements.

Brieter *et al.* [29], from their studied explain that morphology of microporous membrane is very similar in structure and function to a conventional filter as refer to Figure 2.3(b). It has a rigid, highly voided structure with randomly distribute, and interconnected pores. However, these pores differ from those in conventional filter by being extremely small, on the order of 0.01 to 10 μm in diameter. All particles larger than the largest pores are completely rejected by virtue of a sieving effect.

The sponge-like structure of this membrane is homogeneous and isotropic with open surfaces on both wall sides. These membranes achieve reliable, adequate performance and the mechanical stability in term of tensile strength and elongation at break is combined with high reliability and handling safely during the manufacturing process. Figure 2.4 below shows the types of microporous membrane structures.

Mulder [30] in his studied, explain that electrically charged membranes morphology as refer to Figure 2.3(c) can be dense or microporous, but are most commonly very finely microporous, with the pore walls carrying fixed positively charged ions is referred to as an anion-exchange membrane because it binds anions in the surrounding fluid. Similarly, a membrane containing fixed negatively charged ions is called a cation-exchange membrane. Separation with charged membranes is achieved mainly by exclusion of ions of the same charge as the fixed ions of the membrane structure, and to a much lesser extent by the pore size. The separation is affected by the charge and concentration of the ions in solution.

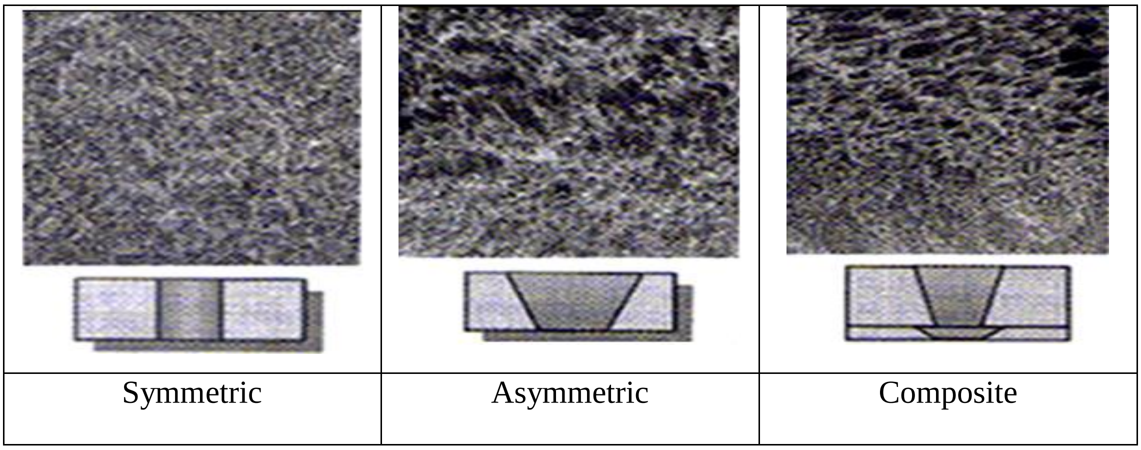


Figure 2.4: Schematic diagram of different membrane morphologies [30]

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