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

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A thesis is submitted in partial fulfillment of the requirement for the award of the Degree of Master of Mechanical Engineering

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SEPTEMBER 2013
Abstract

In developing polymer membranes that respond 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 °C – 395 °C, meanwhile for soft segment at 370 °C – 500 °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 melaluiinya, 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.m\(^3\) 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 \(^{\circ}\)C - 395 \(^{\circ}\)C, sementara bagi segmen lembut pada 370 \(^{\circ}\)C - 500 \(^{\circ}\)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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<td>MDI</td>
<td>4,4’-Methylene-bis-(phenylisocynate)</td>
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<tr>
<td>PEG</td>
<td>Polyethylene glycol</td>
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<tr>
<td>HDMI</td>
<td>Hexamethylene Diisocyanate</td>
</tr>
<tr>
<td>DMF</td>
<td>N,N-dimethylformamide</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>UTM</td>
<td>Universal Testing Machine</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared</td>
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<tr>
<td>TGA</td>
<td>Thermogravimetric</td>
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<tr>
<td>PU</td>
<td>Polyurethane</td>
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<tr>
<td>ºC</td>
<td>Degree Celcius</td>
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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, electrodialysis, 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.
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.

**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.

<table>
<thead>
<tr>
<th>(a) Dense membrane</th>
<th>(b) Microporous membrane</th>
<th>(c) Electrically charged membrane</th>
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<tr>
<td><img src="image" alt="Dense membrane" /></td>
<td><img src="image" alt="Microporous membrane" /></td>
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</table>

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](image-url)
2.2.2 Anisotropic Membranes

According to Koenhen et al. [31], anisotropic membranes are layer structures, changing the porosity and pore size over the whole membrane wall. The anisotropic membranes usually have a very thin surface layer supported on a thick microporous substrate. The thin skin layer is the selective layer to perform separation, while the microporous substrate mainly provides the mechanical strength. Because of the very thin selective layer, the membrane fluxes are very high. Integrally asymmetric membranes, composite membranes and supported liquid membranes are in the category of anisotropic membranes.

<table>
<thead>
<tr>
<th>(a) Supported liquid membrane</th>
<th>(b) Loeb-Sourirajan/Assymetric membrane</th>
<th>(c) Composite</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Supported liquid membrane" /></td>
<td><img src="image2.png" alt="Loeb-Sourirajan/Assymetric membrane" /></td>
<td><img src="image3.png" alt="Composite" /></td>
</tr>
</tbody>
</table>

Figure 2.5: Schematic diagram of different membrane morphologies of anisotropic membrane [31]

In these recent years, interest in membranes formed from less conventional materials has increased as reported [32]. Ceramic membranes, a special class of microporous membranes, are being used in ultrafiltration and microfiltration applications for which solvent resistance and thermal stability are required. Dense metal membranes, particularly palladium membranes, are being considered for the separation of hydrogen from gas mixtures, and supported liquid films as refer to Figure 2.5 (a) are being developed for carrier-facilitated transport processes.

Meanwhile, the asymmetric membranes combine high permeant flow, provided by a very thin selective top layer and a reasonable mechanical stability, resulting from the under laying porous structure as refer to schematic diagram of
different membrane morphologies of anisotropic membrane in Figure 2.5(b). According to Atala et al. [33], an asymmetric structure characterizes most of the presently commercially available membranes, which are now produced from a wide variety of polymers. By the most common method in generation of asymmetric structures in membranes is the “phase-inversion” process.

Most of the presently available membranes are porous or consist of a dense top layer on a porous structure. The preparation of membrane structures with controlled pore size involves several techniques with relatively simple principles, but which are quite tricky.

In Figure 2.5(c), a composite membrane is comprised of more than one material and structure, and it also considered to belong to asymmetric membranes. Such membranes are usually prepared by multistep method. The top and sub layer can be originated from different polymeric materials with different structures, with each layer able to be optimized independently. Usually, the top is a thin dense polymer skin formed over a microporous support substrate. It can be achieved by dip-coating, interfacial polymerization, in-situ polymerization or plasma polymerization.

Tsui et. al [34] has summarized, usually the top layer is the active layer made of high performance polymer that causes the separation of the solutes. This layer has a thickness around 0.15 to 1 μm. This layer on its own has insufficient mechanical strength and requires some support/reinforcement. As such, the desirable reinforcement layer has to be porous material with desirable mechanical properties and should not resist the passage of liquid. Compares with integrally asymmetric membranes, composite membranes usually contain two separated layers with different separation functions and different membrane materials. The porous substrate acts as mechanical support and the skin layer is mainly used for the selective purpose.

2.2.3 Porosity

According to Gupta et al. [35], filtration media in various forms including membranes, woven, nonwoven and particulate beds are used extensively in a wide variety of applications in areas such as biotech, health care, pharmaceutical, food and beverage, power sources and chemical industries. The performance of filtration
media in all of these industries is determined by the pore structure characteristics of the media.

Three kinds of pores are normally found in materials as in Figure 2.6. The closed pores are not accessible while the blind pores terminate within the material. The through pores permit fluid flow through the material and, hence, are the relevant pores for this application. The important pore structure characteristics of filter media are the most constricted through pore diameter, the largest pore diameter, the mean pore diameter, pore shape, pore distribution, pore volume, pore volume distribution, surface area, liquid permeability, gas permeability. Meanwhile influence of operational parameters are such as compressive stress, cyclic compression, pressure, temperature, chemical environment, sample orientation, inhomogeneity and layered or graded structures.

Figure 2.6: Closed, blind and through pores in materials [35]

Porosity contain pores (cavities, channels, interstices) which are deeper than wide. It also either describe the pores, or describe the cell/pore wall.

Figure 2.7: Different types of pores [35]
2.3 Typical Membrane Technique Preparation

There are various techniques available to produce porous polymeric structures. These included: (i) particulate leaching/solvent casting, (ii) gas foaming, (iii) freeze drying, (iv) electrospinning, and (v) phase inversion, to mention but a few as reported [36]. In general for each types of typical membrane technique preparation are as follow:

(i) **Particulate leaching/solvent casting**

The porogen leaching was first patented by Osada et al. [37]. This technique involves dispersing water-soluble particles, such as salt, sugars, or polymer spheres, in a matrix consisting of the scaffold material dissolved in an organic solvent. After solvent evaporation, a composite of the polymer and porogen remains. The composite is then immersed in water until complete dissolution of the porogen occurs, resulting in a porous scaffold.

This technique 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.

(ii) **Gas foaming**

The use of carbon dioxide to create porosity in polymers has been studied by Mikos et al. [38]. This technique avoids the use of organic solvents and high temperatures, which permits incorporation of growth factors during fabrication. Polymers are subjected to high-pressure carbon dioxide (800psi) for 48 h to saturate the polymer with the gas. When the pressure is slowly reduced to atmospheric pressure, carbon dioxide nucleates and grows within the polymer, forming pores.

This is a simple method with suitable range of biomaterials and no special equipment needed which attract a group of studies [39]. Fully interconnecting pores and large pore interconnections can be fabricated. However, one disadvantage of this technique is that many of the resulting pores are closed (e.g., there is lack of pore inner connectivity). Modifications to this technique include combining gas foaming with particulate-leaching, and this resulted more pore inner connectivity.
(iii) Freeze drying

*Gorna et al. [40]* shows, the freeze-drying technique involves creating an emulsion by homogenizing a polymer solvent solution and water. The mixture is then rapidly quenched in liquid nitrogen, and the solvent and water are removed by freeze-drying. Control of processing parameters, such as volume fraction of the dispersed phase, results in control of the porosity.

Advantages of this technique include the ability to control pore size from 15 to 200 microns, the ability to obtain more than 90%, and the possibility of incorporating growth factors within the scaffolds. This technique has been utilized many biocompatible polymers, including PGA, PLLA, PLGA, and PPF blends. Inclusions of polymers like PPF in composite scaffolds is beneficial for adjustment of compressive strength and properties related to hydrophobicity.

According to Holander *et al.* [41], this is a simple method with suitable range of biomaterials and no special equipment needed. Fully interconnecting pores and large pore interconnections can be fabricated. No organic solvents are required. Some researcher using this method to studied about nanopowder of rare earth tungsten for emission materials.

(iv) Electrospinning

Studied from [42], a modern method for creating porous scaffolds composed of nano and microscale biodegradable fibers employs electrostatic fiber spinning, or electrospinning, a technology derived from the electrostatic spraying of polymer coatings. This method had been used by to form microporous, non-woven poly(e-caprolactone) (PCL) scaffolds.

(v) Phase inversion

*Kaushiva et al.* [43] studied, phase inversion is a process one-phase solution containing the membrane polymer transformed by a precipitation/solidification process into two separate phases into separate phases (a polymer-rich solid and polymer-lean liquid phase) as reported [43]. This process is most common used in generation of asymmetric structure in membranes.
According to Bhattacharya et al. [45], the effect of surface properties on the biocompatibility of biomaterials based on the same material; polyurethane membranes with different surface properties were prepared. Phase inversion technique was using as a method to fabricate the membranes. Ulbricht [46] reported that microporous membranes with controlled pore size and structure were produce from biodegradable polyurethane by using the modified phase inversion technique in some studies.

In other cases, some researcher use two different types of phase inversion technique which consisted wet phase inversion method and dry phase inversion method to produces two different types of membranes (asymmetric and dense film). The in-vitro response of human platelets was studied upon adherence to films/membranes of polyurethane with different soft segments was studied [47].

Chalida et al. [48] has summarized, typically for membranes prepared by phase inversion procedure, the properties of casting polymer solution have significant influence on the structure of the resultant membranes. The more viscous the solution, the smaller exchange rate between nonsolvent and solvent in polymer film solution due to the rheological hindrance, thus resulting in membrane structure with smaller pore size.

Most established membrane polymers however were not meet all the performance requirements for a membrane dedicated to a particular application, therefore membrane modifications are gaining rapidly increasing importance. According to Chalida et al. [48] in his studied, based on the preparation of porous ion-exchanged membranes with their characterizations was summarized that from conventional precipitation method which by immersing the nascent polymer membrane the nascent polymer film directly into water bath which casting solution was took around 1min to form nascent film at room temperature.

As shown in Figure 2.6, sPES membranes with different porosities were synthesized using a so-called phase inversion process, namely wet phase inversion (precipitation), or dry phase inversion (solvent evaporation), or the combination of these two processes. The membrane obtained from conventional precipitation method by immersing the nascent polymer film directly into water bath (it took casting solution around 1 min to form nascent film at room temperature.

As refer to Figure 2.8, (a1–3) was highly porous with largest pore size compared to membranes prepared under other conditions. On the other hand, the
membrane obtained from solvent evaporation method exhibited dense and non-porous structure as shown in Figure 2.8 (g1–3).

Typically for membranes prepared by phase inversion procedure, the properties of casting polymer solution have significant influence on the structure of the resultant membranes as reported by Sirkar et al. [49]. The more viscous the solution, the smaller exchange rate between nonsolvent and solvent in polymer film solution due to the rheological hindrance, thus resulting in membrane structure with smaller pore size. If we suddenly immersed the casted film in water bath, the low viscous polymer can be partly dissolved in water and membrane sheet could not be formed.

![Figure 2.8: SEM images of membranes prepared by phase inversion method with different thickness and drying time [48]](image-url)
2.4 Membrane Modification

According to Guo et al. [50], the parameter affecting the process of membranes such as type of solvent, solvent-nonsolvent ratio, polymer concentration in solution, polymer solidification time, and thickness of the polymer solution layer cast on a substrate were investigate. The phase inversion process consists of the induction of phase separation in a previously homogeneous polymer solution either by temperature change, by immersing the solution in a non-solvent bath (wet process) or exposing it to a non-solvent atmosphere (dry process).

As reported by Seymour et al. [51], in the thermal process, a low molecular weight component usually acts as a solvent at high temperature and as a non-solvent at low temperature. It is then removed after formation of the porous structure. Usually the polymer solution is immersed in a non-solvent bath and a solvent-non-solvent exchange leads to phase separation. The polymer-rich phase forms the porous matrix, while the polymer-poor phase gives rise to the pores. The morphology is usually asymmetric, with a selective skin on the surface.

The discussion so far implies that membrane materials are organic polymers and, in fact, the vast majority of membranes used commercially are polymer-based. Furthermore, polymeric membranes were dominating a very broad range of industrial applications due to their following advantages:

(i) different types of polymeric materials are commercially available
(ii) a large variety of different selective barriers: porous, nonporous, charged and affinity, can be prepared by versatile and robust methods
(iii) production of large membrane area with consistent quality is possible on the technical scale at reasonable cost based on reliable manufacturing processes
(iv) Various membrane shapes (flat sheet, hollow-fiber, capillary, tubular, capsule and formats including membrane modules with high packing density modules can be produced.

Therefore, membrane modification is aimed either to minimize undesired interactions, which reduce membrane performance (e.g., membrane fouling), or to introduce additional interactions (e.g., affinity, responsive or catalytic properties) for improving the selectivity or creating and entirely novel separation function. An
increasing number of methods and technologies investigated for polymer surfaces in general are now being adapted to surface functionalization of polymeric membranes in studied by Szwarc [52].

A key feature of a successful surface modification is a synergy between the useful properties of the base membrane and the novel functional layer. In order to achieve a stable effect, chemical modification is preferable over physical modification. Attachment of functional moieties onto a membrane surface by physical principles can be done via following ways:

(i) Adsorption/adhesion – the functional layer is only physically fixed on the base material, and the binding strength can be increased via multiple interactions between functional groups in the macromolecular layer and on the solid surface.

(ii) Interpenetration via mixing between the added functional polymer and the base polymer in an interphase.

(iii) Mechanical interpenetration (macroscopic entanglement) of an added polymer layer and the pore structure of a membrane.

There are several means to modify polymer properties such as blending, grafting, and curing: (a) Blending is the physical mixture of two (or more) polymers to obtain the requisite properties, (b) Curing is polymerization of an oligomer mixture forms a coating which adheres to the substrate by physical forces, and (c) Grafting is a method wherein monomers are covalently bonded (modified) onto the polymer chain as summarized by Kuitian et al. [53]. Curing gives a smooth finish by filling in the valleys in the surface. The schematic representation of the above membrane modification method is as refer to Figure 2.9.
Figure 2.9: Schematic representation of the methods of polymer modification [53]

(a) **Blending**

According to Kuitian *et al.* [54], polymer blends are defined as combination and intimate mixtures of two kinds of two kinds of polymer, with no covalent bonds between them. In most cases, blends are homogeneous on scales larger than several times the wavelengths of visible light. While in principle, the constituents of a blend are separable by physical means. Material prepared in historically usually contain several percent of elastomer, dispersed in plastic matrix, the plastic component predominates.

There are four basic of conception in which the principal methods of mixing two kinds of polymer molecules include; (a) mechanical blending, (b) graft copolymerization, (c) block copolymerization and (d) interpenetration of polymer network. Therefore, the most important characteristic of a polymer blend of two (or more) polymers is the phase behavior in which two basic types of polymer blends; (a) miscible and (b) immiscible as summarized by Kim *et al.* [55].

Miscibility in the context of polymer blends is defined as the degree of mixing yield properties such as glass transition temperature and permeability, expected of a single phase material. It may be homogeneous
down to the molecular level and associated with the negative value of the free energy of mixing and the domain sizes comparable to the dimensions of the macromolecular statistical segment. Concentration fluctuations of miscible polymers would be expected to be of the order of several nanometer. In fact, many blends noted to be miscible show structure of the order of several nanometers when sensitive method [55].

In contrast, the vast majority of polymer pairs are immiscible with one another. There are only few commercially important polymer blends based on miscible and partially miscible (such as miscible within a low range of concentration) polymer pairs. It is seldom possible to mix two or more polymers and create a blend with useful properties [55].

![SEM images](image)

Figure 2.10: SEM images that showed the effect of blending of chitosan with PEG on membrane surface morphology [55]

According to Anbarason et al [56] in his studied about the effect of blending of chitosan with PEG on surface morphology and crystallization, it is well know that chitosan molecules are quite rigid, and the condition of sample preparation normally has marked effect on crystallization. Through this reason, chitosan film could present branch crystal, spherulites an so on.

Since both chitosan and PEG are crystalline structure polymers, they may interact with each other in a certain manner so that the original crystalline structures of each component have been disturb odor partially damaged to a different extent, leading to various crystalline structures of the blend film.
At first, pure chitosan appeared as a slender acicular structure dispersed homogenously as shown in Figure 2.10 (a). With addition of PEG, the surface structure changed markedly. The surface of chitosan appeared more smooth and uniform, in which with addition of PEG as shown in Figure 2.10 (b), the surface of blend film displayed some irregular holes. As a result of migration, many holes were generated on the surface of blend film.

![Figure 2.11: Morphology of PVDF/PEO-b-PMMA polymer membranes [56]](image)

Likewise, Anbarason et al. [57] in his study about the formation of pores is dependent on the mass fraction of PEO-b-PMMA, membranes shows exhibit a large number of small pores as shown in Figure 2.11 (a), but then the pore distribution on the surface of membrane becomes denser with increase of PEO-b-PMMA as shown in micrograph (e). This can be attributed to the high porosity of PVDF/PEO-b-PMMA blend macroporous membranes, in which the pores in the bulk of the membranes are not well interconnected find when PEO-b-PMMA content is low as shown in Figure 2.11 (a–c).

However, the pores become well interconnected when the mass fraction of PEO is about 30% as shown in Figure 2.11 (d). In the solution of
PVDF/DMF/glycerin, with the evaporation of DMF (solvent), the phase separation between PVDF and glycerin (non-solvent) forms a polymer-rich phase and a polymer-poor phase. The former finally forms the polymer matrix, while the latter forms the porous structure.

Instead, when preparing a new polymer blend from immiscible resins, it is necessary to devise a specific strategy for compatibilizing the mixture to provide for optimum physical performance and long-term stability. Although there do exist a very small number of commercial blends of immiscible polymers that are not compatibilized, most commercially available blends of immiscible polymers have been compatibilized by some specific mechanism.

Polymer blends like low molecular weight solvents can exhibit miscibility or phase separation and various levels of mixing in between the extremes such as partial miscibility. The most important factor leading to miscibility in low molecular weight materials is the combinatorial entropy contribution which is very large compared to high molecular weight polymers. This contribution is the reason that solvent-solvent mixtures offer a much broader range of miscibility than polymer-solvent combinations. The range of miscible combinations involving polymer-polymer mixtures is even much smaller [58-59].

Due to some disadvantages such as poor mechanical properties of polymers from renewable resources, or to offset the high price of synthetic biodegradable polymers, various blend and have been developed. Blends comprises of three kinds of polymers from renewable resources [60]:

(i) Natural polymers, such as starch, protein and cellulose.
(ii) Synthetic polymers from natural monomers, such as polylactic acid.
(iii) Polymers from microbial fermentation, such as polyhydroxybutyrate are described with an emphasis on potential applications.

The majority of polymer blends containing elastomeric, thermoplastic, liquid crystalline polymers are processed by melt extrusion at some point. After melt extrusion with intensive mixing, the morphology of an immiscible polymer blend on a microscopic scale will often consist of a dispersed phase of the more viscous polymer in a continuous matrix of less viscous polymer
depending upon relative amounts and viscosities of the two polymers in blend as referred to Wang et al. [61].

The formation of optimum dispersed phase particle size and long-term stabilization of blend morphology are critical if the blends is to have optimum properties and in particular good mechanical properties. If this morphology is not stabilized, then the dispersed phase may coalesce during any subsequent heat and high stress treatment such as injection molding [62].

According to Samal et al. [63], an important aspect of all compatibilization strategies is the promotion of morphology stabilization. It be provided by sufficient interfacial adhesion and lowered interfacial tension between the two polymer phases of the various compatibilization strategies that have been devised an increasingly common method is either to add a block, graft, or crosslinked copolymer of the two (or more) separate polymers in the blend or to form such copolymer through covalent or ionic bond formation during “Reactive Compatibilization” step.

Blends are usually made in two ways; (1) The first way is to dissolve two polymers in the same solvent, and the (2) second way wait for the solvent to evaporate and just eft with a blend at the bottom in beaker, presuming that two polymers are miscible.

According to Bhattacharya [64], the basic strategies for “Reactive Compatibilization” of two-phase polymer blends can divide into at least three major categories:

(i) Co-crystallization of two phases
This particular strategy is limited to those cases in which an immiscible polymer blend contains two semi-crystallize. It may also occur as a secondary process in an intimately mixed blend containing a copolymer with concomitant effects on blend properties [65].

(ii) In situ Immobilization of one phase: Dynamic Vulcanization
In these cases, a dispersed phase of cross linkable rubber is vulcanizable in the presence of a matrix of a second, immiscible, non-vulcanizable polymer during the residence time of melt processing. There are five key requirements for preparing optimum composition by dynamic vulcanization [66].
(i) Good match between surfaces energies of the dispersed phase and the matrix.
(ii) Low entanglement molecular length (high entanglement density) of the rubber.
(iii) Crystalline plastic matrix.
(iv) Stable rubber and plastic at blend processing
(v) Availability of appropriate curing system for rubber under desired processing conditions.

(iii) Addition of a third material as a compatibilizing agent
There are two basic options for addition of a copolymer compatibilizer to a blend of immiscible polymers:

- Addition of a separate compatibilizing agent
  The copolymer can be synthesized in a separate step followed by addition to the blend. It may be a third material which not derived from either of the two immiscible polymers. This is also chemically unreactive analog of one or both of the two immiscible polymers that has an attractive interaction with each polymer [67].

- Addition of a copolymer of the two immiscible polymers
  Adding a copolymer to a blend of immiscible polymers is to form the copolymer in situ which most economical and efficient process for a chemical reaction during the extrusion process during establishment of the immiscible phase morphology (Reactive Compatibilization).

  Sanli et al. [68] reported that this manner is very ideal suited to act as compatibilizing agent for an immiscible blend, where if the copolymer is at the interface of the two phases, then the segments of the copolymer dissolve in the respective bulk phases of the same identity. The copolymer acts as emulsifying agent for the blend resulting in reduced interfacial energy and improved interphase adhesion.
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