PRELIMINARY FABRICATION OF BIODEGRADABLE POLYMER MEMBRANES FROM RENEWABLE RESOURCES

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ABSTRACT

A membrane is an interphase between two adjacent phases acting as a selective barrier, regulating the transport substances between the two components. Microporous membranes with controlled pore size and structure were produce from biodegradable polymer based on vegetable oil monomer using phase inversion technique. The optimal conditions for the preparation of microporous polymer membranes was polymer concentrations in N,N-dimethylformamide (DMF) solution 12% (w/v), 15% (w/v), 18% (w/v) and 21% (w/v). The result, the membranes show two types of structure: pinhole-like structure and interconnected network structure. The structure of the membranes consisted of thick fibrillar elements. The membrane cross-section seemed to be composed of stacks of separate layers. Permeability of the polymer membranes obtained at lower concentrations, exhibit extremely higher water permeability with value 0.160952, 0.01482, 0.00098 and 0.00051 L/s.m^3 for 12%, 15%, 18% and 21% (w/v) respectively. As the concentration increases, the surface layer of the membranes becomes thicker. Thus, the membranes are easily break compared to the membranes that have densely packed as shown by tear test of 12%, 15%, 18%, and 21% (w/v) with 21.8495 N/mm, 13.9566 N/mm, 10.5433 N/mm, and 12.1662 N/mm tear strength respectively. The fabrication of the polymer membranes with the structure and permeability properties was successfully conducted achieved as a novel research as indicated in many work. Applications of these polymer membranes are use for water treatment, skin wound cover and, in combination with autogenous chondrocytes, as an ‘artificial periosteum’ in the treatment of cartilage defects.

ABSTRAK

Membran merupakan alat pemisah iaitu penghalang yang bersifat selektif yang dapat memisahkan dua fasa dari berbagai campuran. Membran berpori dengan saiz pori dan struktur terkawal dihasilkan daripada polimer terbiodegradasikan menggunakan monomer minyak sayur menggunakan teknik penyongsangan fasa. Kondisi optimum bagi menyediakan membran polimer berpori adalah kepekatan yang berbeza di dalam cairan N,N-dimethylformamide, DMF iaitu 12%, 15%, 18%, dan 21% (w/v). Hasil analisa daripada Mikroskop Elekton Imbasan (SEM), membran tersebut menunujukkan dua struktur berbeza yang terhasil iaitu struktur berbentuk lubang jarum dan rangkaian bertaup. Struktur membran tersebut terdiri daripada unsur *fibrillar* yang tebal. Struktur di bahagian rentas pula menunjukkan terdapat tindanan lapisan yang berasingan. Sifat kebolehtelapan membran polimer diperoleh pada kepekatan rendah mempamerkan ketelapan terhadap air yang sangat tinggi iaitu 0.160952, 0.01482, 0.00098 dan 0.00051 L/s.m^3 masing-masing pada kepekatan 12%, 15%, 18%, dan 21% (w/v). Apabila kepekatan meningkat, lapisan permukaan menjadi lebih tebal dan menyebabkan membran mudah terkoyak berbanding dengan membran yang padat seperti yang ditunjukkan dalam analisa kekuatan koyakan untuk membran berpekatan 12%, 15%, 18%, dan 21% (w/v) di mana masing-masing memberi nilai 21.8495 N/mm, 13.9566 N/mm, 10.5433 N/mm, dan 12.1662 N/mm. Fabrikasi membran dengan struktur, sifat kebolehtelapan terhadap air dan sifat mekanikal yang diperoleh telah vonesva dicapai sejajar dengan penyelidikan-penyelidikan terkini. Membran polimer ini dapat diaplikasikan dalam proses terapi air, penggantian kulit, dan kecacatan tulang rawan.

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LIST OF SYMBOLS

MDI : 4,4’-Methylen-bis-(phenylisocynate)
DMF : N,N-dimethylformamide
SEM : Scanning Electron Microscope
UTM : Universal Testing Machine
PU : Polyurethane
ºC : Degree Celcius

CHAPTER 1

INTRODUCTION

1.1 Research Background

In recent years, membranes technology has been seen as an alternative approach to the conventional process for separation applications because of the low cost and energy consumption, simple operation and the inherent of the membrane process characteristics. The worldwide sales of synthetic membranes was estimated at over United States $2 billion (Srikanth, 2003). The incorporation of renewable resources from the vegetable oils to form polyols in polyurethane membrane lead to new materials with outstanding mechanical properties encompassing the surface structure and the permeability properties of the membranes.

A few techniques such as salt leaching, phase separation, gas foaming, freeze drying, electrostatic spinning and solid free form fabrication have been develop to generate highly porous polymeric structures (Srikanth, 2003) . Phase inversion is a process whereby a polymer is transformed in a controlled manner from a liquid to a solid state (Zhang *et al.*, 1999). It can be initiated by solvent evaporation, thermal precipitation or precipitation with nonsolvent, the latter being especially well suited for the fabrication of microporous polymer membranes (Klempner & Frisch, 1991).

In this process, interdiffusion of the solvent with the nonsolvent results in the decomposition of polymer solution into a polymer-rich phase and a polymer-poor phase. Biodegradable polymer-rich phase is solidified into a solid matrix, while the polymer-poor phase forms the pores. Depending on the conditions of phase-inversion the porous polymeric structures formed will differ in pore size, geometry, distribution and interconnectivity.

This study addresses the design of biodegradable microporous polymer membranes for separation applications using the modified phase-inverse technique. Microporous membranes can be produces from biodegradable polymer from renewable resources based on diisocyanate. The parameter affecting the process of membrane formation will be investigated based on the polymer concentration. From the system evaluated, the best results obtained for the system will be identified. Potential applications of these membranes are use for water treatment, skin wound cover and, in combination with autogenous chondrocytes, as an 'artificial periosteum' in the treatment of cartilage defects.

1.2 Problem Statement

i. As the petroleum-based synthetic polymers are widely used in industry, it becomes a burden to the environmental because they do not degrade as they use of non-renewable fossil based petrochemical feedstock. This attracts the scientist to searching for new raw materials such as vegetable oils which are offered renewable resources environmentally friendly.

ii. To date, the increasing demand of industrial raw materials to use the renewable resources have brought vegetable oils into focus as a potential source of raw materials because of their potential to substitute petrochemical derivatives. The term renewable resources giving definition that the agricultural products such as cellulose and starch and glycerol ester of fats and oils are synthesized by the solar energy.

iii. Membrane technology is a major importance in a variety in tissue engineering and separation applications. It is now been industrially establish in impressively large scale after a long period through the producing of biological membrane

(Baker, 2004). Vegetable oil is one of the most valuable to develop as raw materials for membrane. Its offer advantages such as low cost, acceptable specific properties, biodegradability and availability of renewable resources.

1.3 Research Aim

i. To produces microporous membranes from biodegradable polymer synthesized from vegetable oil and modified the morphology structure using phase inversion technique by using different parameters: type of solvent, solvent-nonsolvent ratio, polymer concentration in solution, polymer solidification time, and polymer solution layer cast on a substrate.
ii. To achieved the structure and permeability properties as the same as the novelty research before.

1.4 Objectives of Study

- To investigate the potential of biodegradable polymer synthesized from vegetable oil to be used and modified using phase inversion technique for preliminary fabrication of membranes
- To make the best recommendation based on polymer concentration in solution (12, 15, 18 and 21% w/v) in order to create interconnected pores, well defined pore size and structure, good water permeability and sufficient tear strength membranes.

1.5 Scope of Study

This study addresses the design of biodegradable microporous polymer membranes for separation applications using modified phase-inversion technique from renewable resources. The fabrication of different polymer concentration in solution (12%, 15 %, 18% and 21% w/v) of the membranes by using different concentration of non-solvent to dilute the polymer. The Scanning Electron Microscopy (SEM) is used to determine the structure of the polymer membrane and compared with the novelty research before. This membranes were also evaluated by undergo several testing including tear test and water permeability.

CHAPTER 2

LITERATURE REVIEW

2.1 Polymers

A polymer is a substance composed of molecules characterized by the multiple repetitions of one or more species of atoms or group of atoms linked to each other (Gedde, 1995). The word polymer originates from Greek words ‘poly’ literally means ‘many parts’ (Smith & Hashemi, 2006). To form a solid, a polymeric solid material may be considered to be one that contains many chemical units that are bonded together.

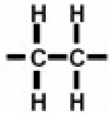
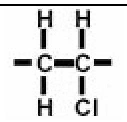
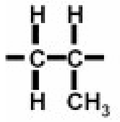
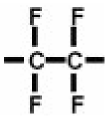
Polymer can be divided into two groups: (1) Natural Polymer such as cotton, starch, proteins, and wool and (2) Synthetic polymer such as nylon, poly (vinyl chloride), polystyrene, polytherimide and etc (Sperling, 2006). Table 2.1 represented the common polymers with their constitutional repeating units and uses.

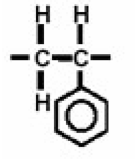
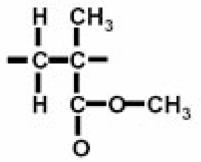
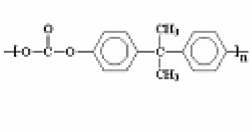
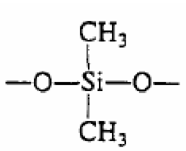
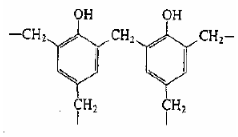
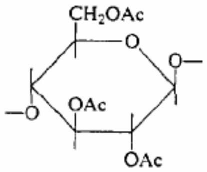
On the other hand, biopolymers are polymer produced by living organism either biological (non-fossil) in origin, or susceptible to digestion by microorganism or chemical breakdown in the environment such as hydrolysis or it can be both process. It contains monomeric units that are covalently bonded to form large structures and can be classified into three classes: polynucleotides, polypeptides and polysaccharides. Polysaccharides include cellulose, starch, the carbohydrate polymers produce by bacteria and fungi and animal-protein-based biopolymer such as wool, silk, gelatin and collagen.

Rising crude oil process and requirement for an environmentally responsible end of life disposal routes for polymer manufacture force us to search the alternative resources. Thus, synthetic biopolymer has been developed to perceive uncertainly in the continuing supply of fossil raw materials. The primary advantages of natural origin materials over conventional polymers can be included as the following (Johnson, 2003):

i. Non-fossil origin raw materials
ii. Sequestering of atmospheric CO_2
iii. No requirement for an extensive and costly recovery and separation infrastructure for recycling
iv. Service life is equivalent to fossil origin polymers
v. Decrease the oil and gas dependence, price and availability

Table 2.1: Constitutional repeating units of common polymer

Polymer	Symbol	Type of Polymerization	Polymer	Uses
Polyethylene	PE	addition	 $-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-$	Electrical insulation, bottles and toys, plastic bags
Polyvinyl chloride	PVC	addition	 $-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{Cl}{C}}-$	Pipes and flooring
Polypropylene	PP	addition	 $-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{CH_3}{C}}-$	Packaging, textiles, and laboratory equipment
Polytetrafluoroethylene	PTFE	addition	 $-\overset{F}{\underset{F}{C}}-\overset{F}{\underset{F}{C}}-$	Non-stick surfaces electrical insulation

Polystyrene	PS	addition		Toys and cabinet packaging
Polymethyl methacrylate	PMMA	addition		Lighting covers and sign skylight
Polycarbonate	PC	condensation		Electric component, construction materials and automotive
Silicones		condensation		Water repellent coating and rubber
Phenol formaldehyde	PF	condensation		Mixed with filler, molded electric case, adhesives, laminates and varnishes
Cellulose acetate		condensation		Photographic film

2.2 Polymer based on renewable materials

The raw materials to produce the polymer are commonly derived from the petroleum oil and natural gas. As the rising crude oil prices and effects of using petroleum based polymer to the environmental has lead us to find the alternatives of energy sources. Recently, the use of renewable resource has attracted the attention of many researchers. The term ‘renewable resource’ is defined as any animal or vegetable species which is exploited without endangering its survival and which is renewed by synthesizes of sunlight (Belgacem, & Gandini, 2008).

According to the researcher before (Narine & Kong, 2005), polysaccharides are the most well-known and widely use of renewable resources which are consist of starches, cellulose, and chitin/chitosan. Others resources are from proteins and natural fats and oils.

2.2.1 Starch

Starch is extremely abundant edible polysaccharides present in a wide variety of tubers and cereal grains such as rice and seeds (corn). It composed of two macromolecules bearing the same structural units, 1,4-D-glucopyranose in linear and highly branches architecture which is present in different proportions according to the species that produces it as shown in Figure 2.1a and 2.1b (Belgacem, & Gandini, 2008).

The starch molecule is heavily hydrated as it contains many exposed hydroxyl groups, which form hydrogen bonds on coming into contact with water. From Figure 2.1a, it shows that the starch molecule contains two important functional groups; -OH groups for substitution reactions and C-O-C is susceptible to chain breakage. This two features lead to the synthesis of biodegradable plastics.

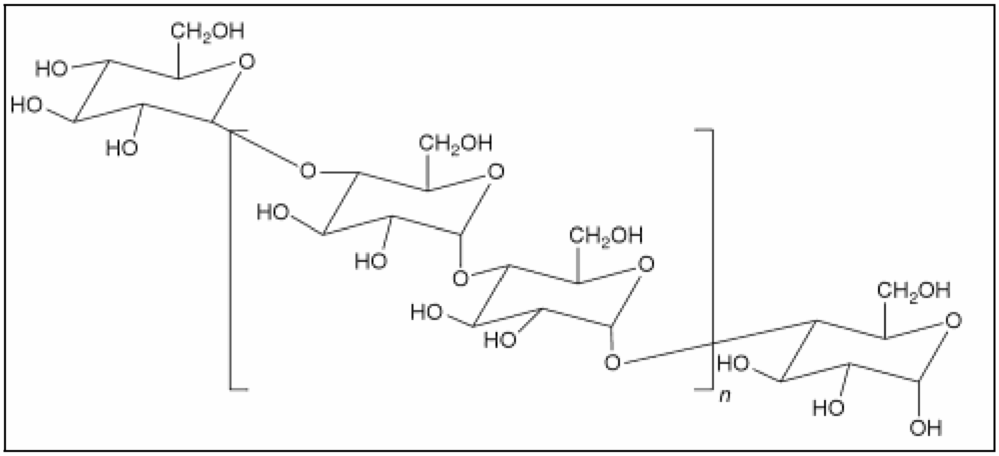


Figure 2.1a: Macromolecular component of starch – amylase (Belgacem, & Gandini, 2008).

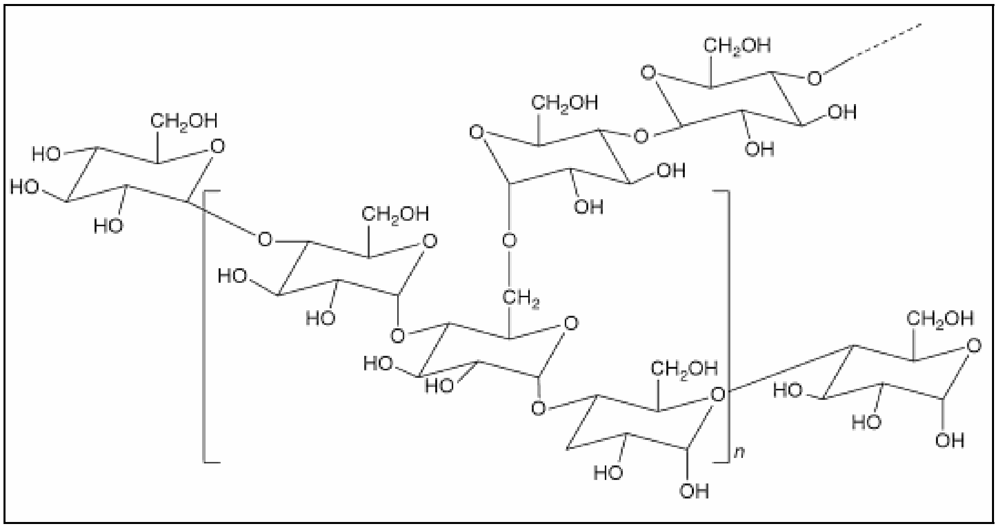


Figure 2.1b: Macromolecular component of starch – amylopectin(Belgacem, & Gandini, 2008).

2.2.2 Cellulose

Cellulose is a linear, unbranched homopolysaccharide and resembles amylase, which is the primary polymeric constituent of starch. Figure 2.2 shows the structure of cellulose. Cellulose is the most common organic compound consists of formula $(C_6H_{10}O_5)_n$. It is the structural component of the primary cell wall of greenplants, algae and oomycetes. Unlike starch, there occurs no branching on the molecules adopt an extended and stiff rod-like conformation, aided by the equatorial conformation of the glucose residues. Cellulose is receiving interest as a source of novel materials because of its properties (Kaith & Kaur, 2011):

- The chemical bulk modification for the preparation of original macromolecular derivatives with specific functional properties.
- The surface modification of cellulose fibres in view of their use as reinforcing elements in composite materials and as high-tech components.
- The technology and applications associated with bacterial cellulose.
- The processing and characterization of these composites, including the use of nano fibres.

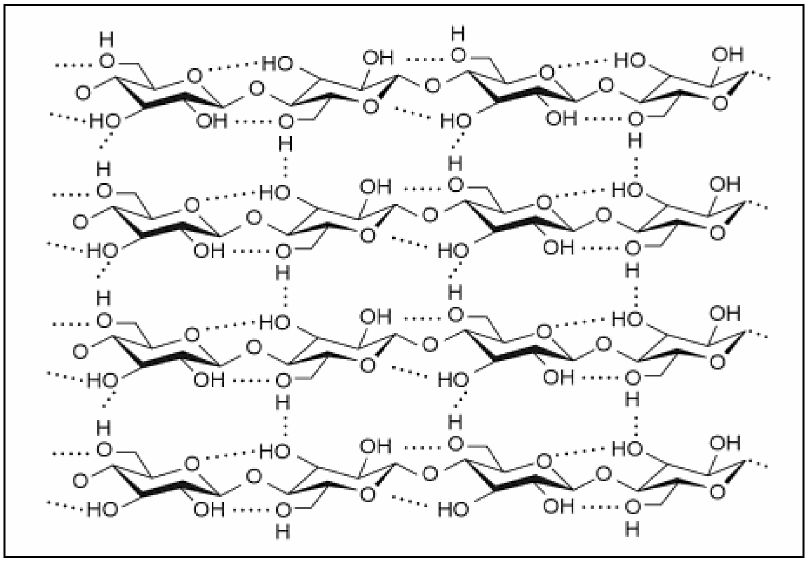


Figure 2.2: Structure of cellulose (Burdick & Mauck, 2011).

2.2.3 Chitin and Chitosan

Chitin and chitosan is considered as a second most abundant polymer present in biomass after cellulose. Chitin and chitosan are biocompatible and biodegradable natural polymers, used in biomedical applications and cosmetics. Chitosan (poly D-glucosmine) is derived from chitin (poly-N-acetyl-D-glucosamine), a polysaccharide formed in shellfish exoskeleton, which has received more attention in biomaterial development than chitin due to its solubility. Chitin and chitosan are functionally useful polymers due to the mechanical properties of films and fibers, low oxygen permeability of films and in the case of chitosan, ease of solubilization in dilute acetic acid (Kaplan, 1998).

Various reaction mechanisms can be used to form sugar-bond chitosans such as galactosylated chitosan, which support hepatocyte culture, or mannosylated chitosan, which is specifically recognized by antigen-presenting cells. Lastly, sulfonation of either the amino or hydroxyl groups of chitosan yields a polymer that bears a close structural resemblance to heparin (Burdick & Mauck, 2011).

Chitosan membranes and fibers have excellent neurological cell affinity. They are promising materials for nerve repair. They could be improved by incorporation with neurotrophic factors and neural cells (Yuan *et al*., 2004).

Applications for chitin and chitosan include water and effluent treatments as a coagulant and chelating agent; paper manufacture as a wet strength additive; medical and pharmaceutical uses (synthetic skin, surgical sutures, contact lenses); textile industry uses as a coating and in blends; cosmetics and food industry as a livestock feed and stabilizer for emulsions. Figure 2.3 shows the structure of chitosan.

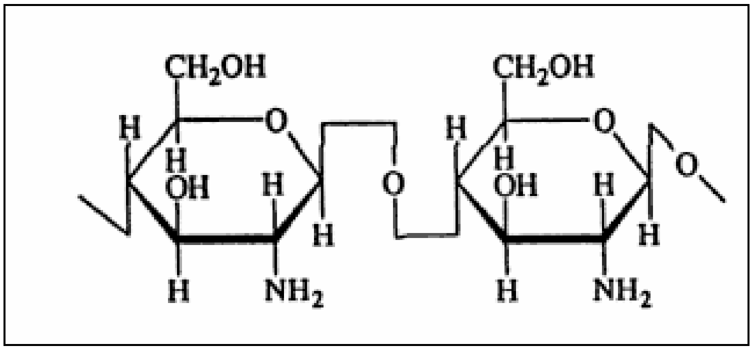


Figure 2.3: Structure of chitosan (Burdick & Mauck, 2011).

2.2.4 Proteins

There are many types of protein that can be divided into some classification according to the sources of the proteins. For examples, soy, zein, and wheat gluten are derived from plants. Casein is a protein mixture derived from mammal's milk. Most of these materials are good oxygen barriers although their hydrophilic nature results in poor moisture except the zein proteins (Kaplan, 1998).

Collagen is a major structural protein in animal tissue found in skin, bone and connective tissues of mammals. It is the most abundant protein in the animal kingdom. Collagen forms a characteristic triple helix where all chains are in parallel alignment as shown in Figure 2.4. Like any other protein, collagen is susceptible to depolymerization due to the action of variety of protease enzymes. Applications of collagen are used primarily in medical applications (tissue nerve repair, wound dressing, drug delivery, and vascular graft) and in food as casing materials.

Gelatin is an animal byproduct derived from the partial hydrolysis of collagen followed by hot water extraction. Gelatin can be readily crosslinked, biodegradable, soluble in water, acetic acid and polyhydric alcohols and insoluble in most organic solvents. Applications of gelatin are used extensively in the food, pharmaceutical and photographic industries. It is also can be used in fibers with the incorporation of plasticizers.

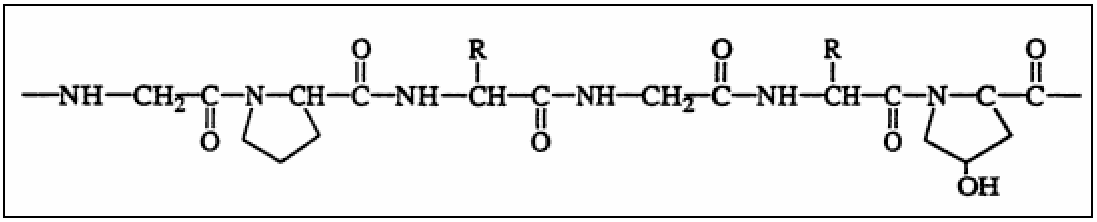


Figure 2.4: Structure of collagen segment (Kaplan, 1998).

2.3 Vegetable oil as renewable resources

In recent years, there has been growing trend of using vegetable oils as raw materials as it giving many advantages; the vegetable oils are renewable, long fatty acid chains of vegetable oils impart desirable flexibility and toughness to other brittle resin (epoxy, urethane and polyester resin) and products derived from vegetable oils and fats are more readily biodegradable. The use of vegetable fats and oils allows the development of competitive, powerful products which are both consumer-friendly and environment-friendly (Hill, 2000). There are five major sources of vegetable oils: soybean, oil palm, rapeseed, sunflower and coconut. Approximately 80% of the global oil and fat production is vegetable oil, whereas 20% is of animal origin. Figure 2.5a shows the world production and uses of oils and fats.

Vegetable oils are triglycerides (tri-esters of glycerol with long chain fatty acids) with varying composition of fatty acids depending on the plant, season, crop and growing conditions. The word ‘oil’ is refers to the triglycerides that are in liquid form at room temperature (Meier *et al.*, 2007).

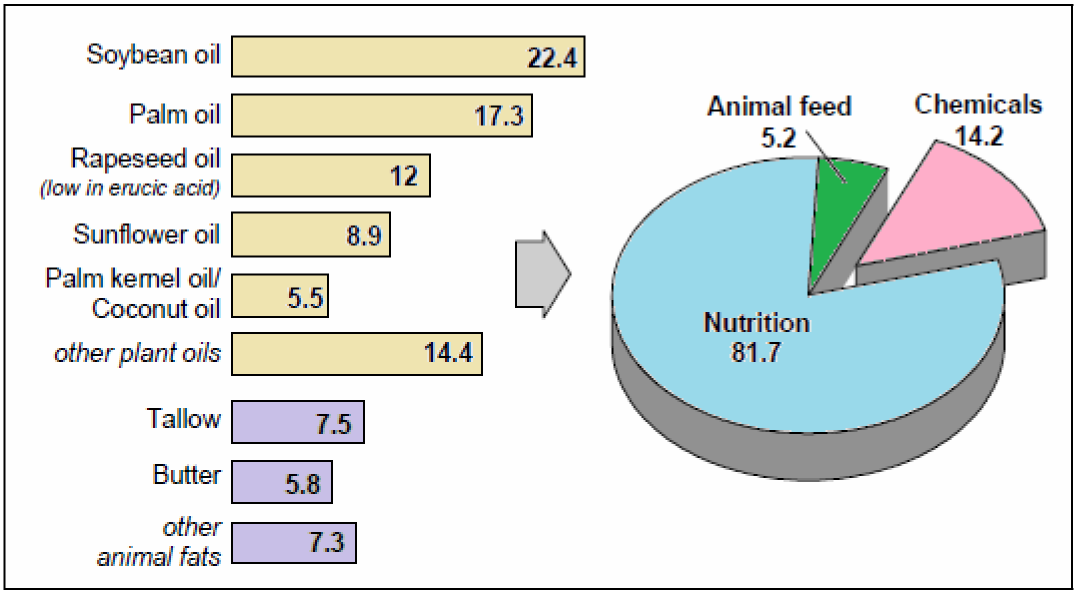


Figure 2.5a: World production and uses of oils and fats (1998, in million 14ones) [acc. To Oil World, Hamburg].

Figure 2.5b shows on overview of some fatty acid for chemical modification and synthesis of fine chemicals, monomers and polymers (Metzger & Bornscheuer, 2006). Oleic acid (1) are derived from new sunflower, linoleic acid (2) derived from soybean, linolenic acid (3) derived from linseed, petroselinic acid (4) derived from Coriandrum sativum, erucic acid (5) derived from rape seed, calendic acid (6) derived from Calendula officinalis, α-eleostearic acid (7) derived from tung oil, vernolic acid (8) derived from Vernonia galamensis, and ricinoelic acid (9) derived from castor oil.

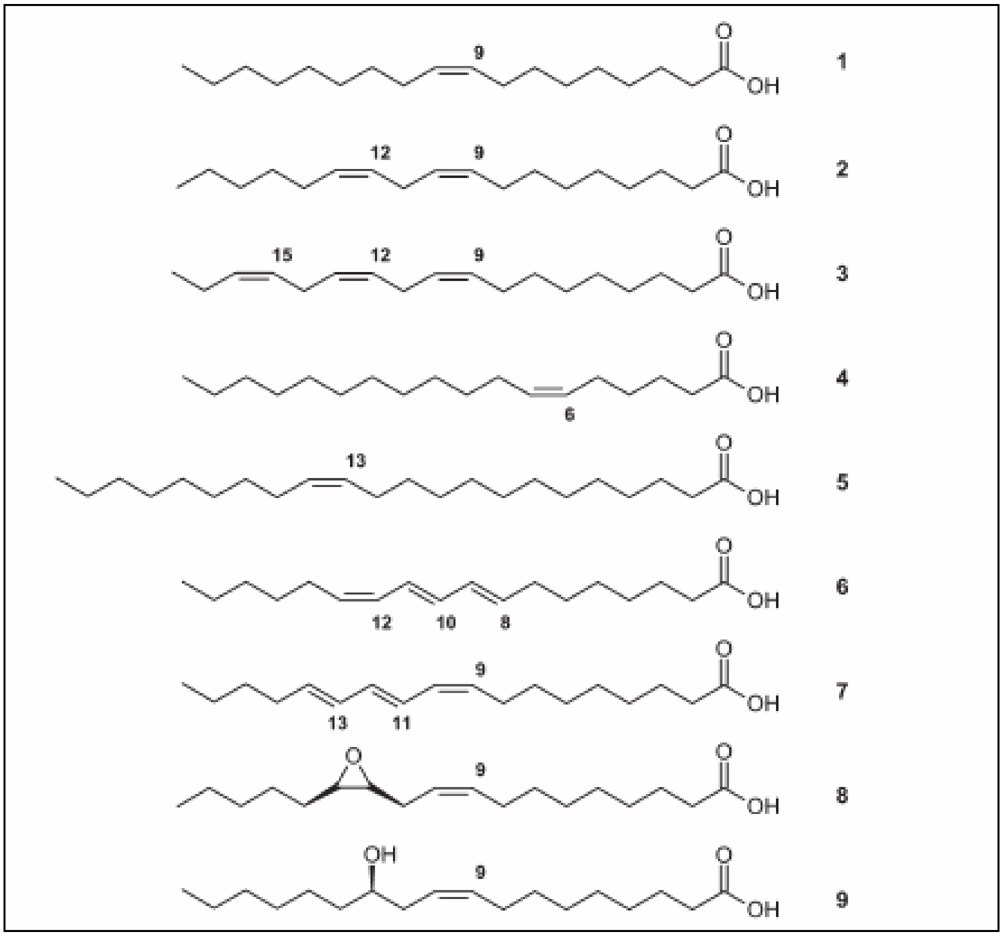


Figure 2.5b: Fatty acids as starting materials for the synthesis of novel fatty compounds: (1) oleic acid, (2) linoleic acid, (3) linolenic acid, (4) petroselinic acid, (5) erucic acid, (6) calendic acid, (7) α-eleostearic acid, (8) vernolic acid, (9) ricinoelic acid (Metzger & Bornscheuer, 2006).

2.4 Polyurethane (PU)

Polyurethanes are large family of synthetic polymers that are composed of alternating soft polyether segments, most commonly long linear polyether, and hard segments consisting of urethane linkages and aromatic group which is formed from the extension of diisocyanate. The existence of microphase separation was caused by clustering of some of the hard and soft segments into separate domain (Seymour & Cooper, 1972). Figure 2.6a shows the segments in polyurethane.

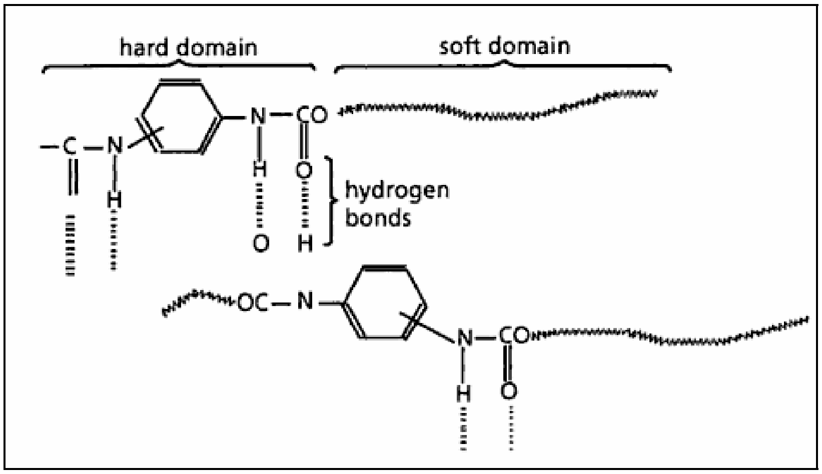


Figure 2.6a: Hard segment and soft segments of polyurethane elastomer (Seymour & Cooper, 1972).

Polyurethane materials have many applications especially in medical applications and tissue engineering which require stable mechanical properties of structural integrity (heart valves, vascular prostheses, blood filters, and artificial skin materials) because of their good mechanical properties and chemical resistance, such as tensile strength, abrasion, oil resistance, long fatigue life, elastic and good blood compatibility (Kim *et al.*, 2005).

Galland and Lam (1993) had studied that the properties of polyurethane are greatly influenced by the degree of microphase separation. Currently, non-toxic, biodegradable lysine-di-isocynate (LDI) based on polyurethanes are being developed for uses in tissue engineering (Zhang *et al.*, 2000). Figure 2.6b shows the cross linking of polyurethane elastomer.

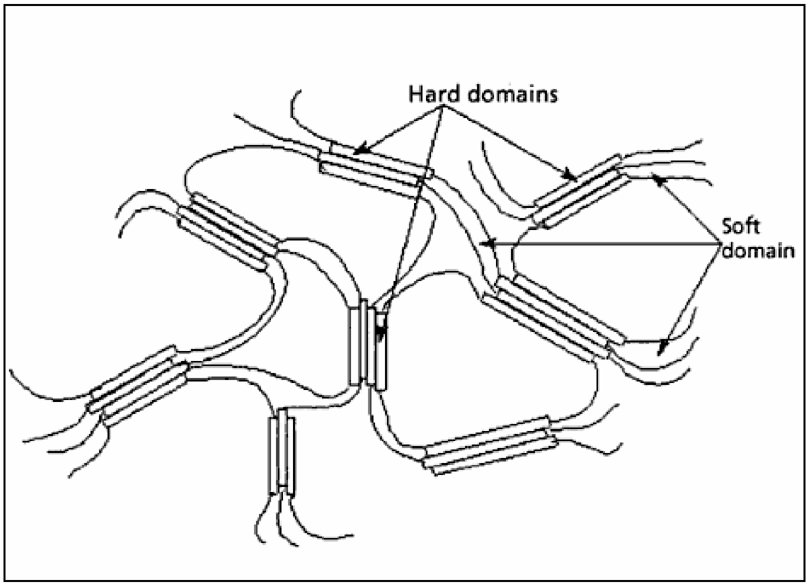


Figure 2.6b: Virtually crosslinked of polyurethane elastomer (Seymour & Cooper, 1972).

2.4.1 Polyurethane from renewable resources

Natural polymers having more than two hydroxyl groups per molecule which can be used as polyols for polyurethanes preparation provides that an efficient reaction with isocynates.

Several attemps have been use plant-based component as raw materials to synthesized polyurethanes. Some group of researcher had prepared polyurethanes from lignins and the thermal and mechanical properties of the polymer had been studied (Nakamura *et al*., 1991 & Yoshida *et al*., 1990).

Those studies indicate that the plant component act as hard segments in those polyurethanes and the thermal and mechanical properties can be controlled by changing the amounts of hard and soft segments.

Polyurethane can be degrades in several ways, hydrolysis, photolysis, solvolysis, thermolysis, pyrolysis, biologically-induced environmental stress cracking, oxidation and microbial (Liu, 2000). It can degrade in vivo and produce toxic, carcinogenic, and mutagenic aromatic diamines. Accordingly extensive research was employed to determine the biodegradability properties of polyurethanes in order to improve their biostability. On the other hand, this observation opens the door for polyurethane in a brand-new area, tissue engineering, where controlled degradation is required (Burdick, & Mauck, 2011).

2.5 Membrane of polymeric materials

A membrane is an interphase between two adjacent phases acting as a selective barrier, regulating the transport of substances between the two components (Mulder, 1996). 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 (Scoft, 1998).

Membranes may be homogeneous or heterogeneous, symmetrical or asymmetrical, and porous or non-porous (Nunas, & Peineman, 2006). They can be organic or inorganic, liquid or solid. Membranes can be classified, according to their morphology as shown in Figure 2.7a. 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 (Nath, 2008).

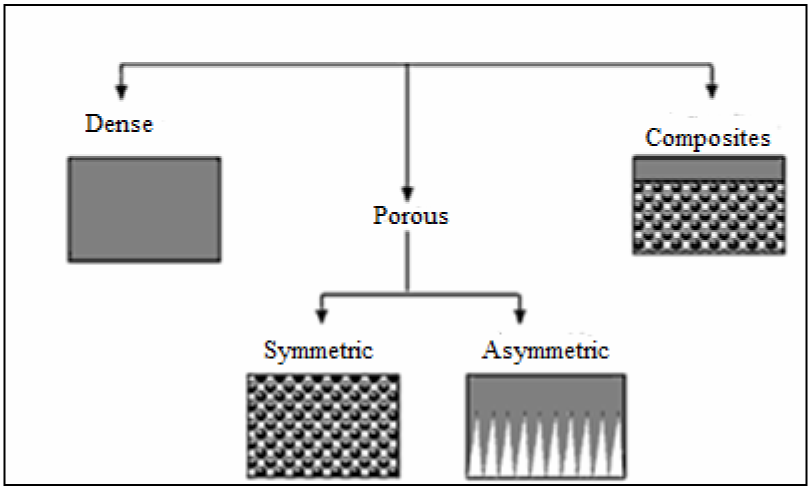


Figure 2.7a: Membrane classification according to the morphology (Nunas, & Peineman, 2006).

Membranes are generally classified by the nature of the materials, the membrane morphology, geometry, preparation method, separation regime and process. Based on the membrane materials, membranes are grouped into polymeric and inorganic membranes. For polymeric membranes, many organic polymers including crystalline and amorphous, glassy and rubbery, are suitable for the membrane fabrication (Wang & Chen *et al.*, 2010). The preparation methods involve phase inversion, interfacial reaction, coating, stretching, etc. Figure 2.7b shows the membrane preparation according to the membrane classification.

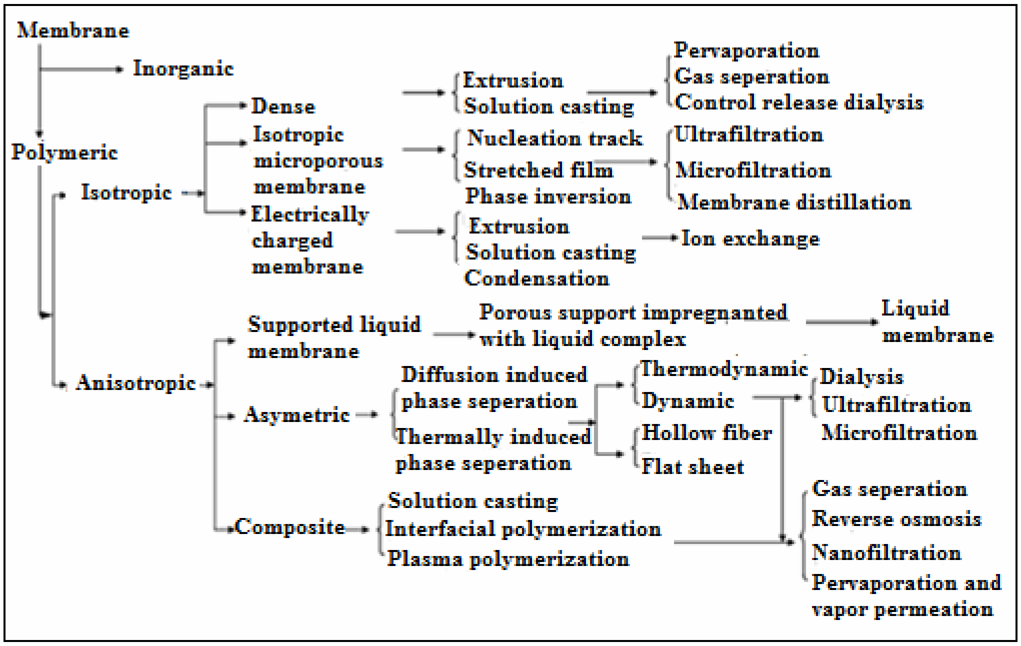


Figure 2.7b: Membrane classification (Wang & Chen *et al.*, 2010).

Transport through a membrane can be affected by convection or by diffusion of individual molecules induced by an electric field or concentration, pressure or temperature gradient. Membranes can also physically or chemically modify the permeating species (as with ion exchange or biofunctional membranes), prevent permeation (eg. In packaging or coating applications) or regulate the rate of permeation (as in controlled drug delivery) (Peinemann, & Nunes, 2008). Thus, membrane maybe either passive or active, it depends upon the membrane’s ability to alter chemical nature of the permeating species.

2.6 Types of membranes

2.6.1 Isotropic Membranes

Dense membranes are 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. 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.

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 (Wang & Chen *et al.*, 2010). Figure 2.8 shows the schematic diagram of different membrane morphologies.

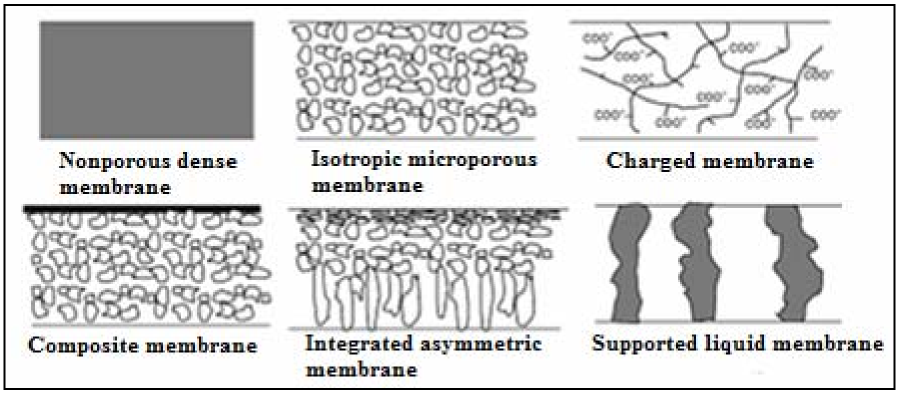


Figure 2.8: Schematic diagram of different membrane morphologies (Wang & Chen *et al.*, 2010).

2.6.1.1 Microporous Membranes

A microporous membrane is very similar in structure and function to a conventional filter. 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 (Nath, 2008).

2.6.1.2 Non-Porous, Dense Membranes

Nonporous, dense membranes consist of a dense film through which permeants 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.

2.6.1.3 Electrically Charged Membranes

Electrically charged membranes 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. For example, monovalent ions are excluded less effectively than divalent ions and, in solutions of high ionic strength, selectively decreases. Electrically charged membranes are used for processing electrolyte solutions in electrodialysis.

2.6.2 Anisotropic Membranes

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.

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.

2.7 Theoretical approach to membrane formation

The formation of the membranes was described through the phase diagram as shown in Figure 2.9a whereby the path starts with a point representing the original casting solution and finishes at appoint representing the final composition of the final membrane (Baker, 2004).

Figure 2.9a and Figure 2.9b represent the three components – polymer, solvent and non-solvent, meanwhile points within the triangle represents mixtures of the three components. The diagram shows two principle regions: (1) one-phase region, which all components are miscible and (2) two-phase region which the systems separate into a solid (polymer-rich) and a liquid (polymer-poor) phase. The casting solutions moves from one phase region to two phase region which the solution loses solvent and gain non-solvent during the precipitation. The membrane precipitation process can be divided into series of steps:

1. The polymer phase that separates on the precipitation may be in form of liquid or semi-liquid gel. At this point, the precipitation domains may be able to flow and agglomerates.
2. The polymer converts to relatively solid gel phase and forms the matrix of the final membranes. The liquid solvent and non-solvent phase forms the pores.

Figure 2.9b is present the process of membrane formation as line through the phase diagram which is approach by researcher before (Strathmann *et al*., 1985). From the diagram A is represents the initial casting solution composition, D represents the final membrane composition which the two-phase are in equilibrium: a solid (polymer-rich) phase that forms the matrix of the final membrane. This composition is represents in the diagram as point S. Meanwhile, L represents a liquid (polymer-poor) phase which membrane pores filled with precipitant are contributes here.

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