CHAPTER I

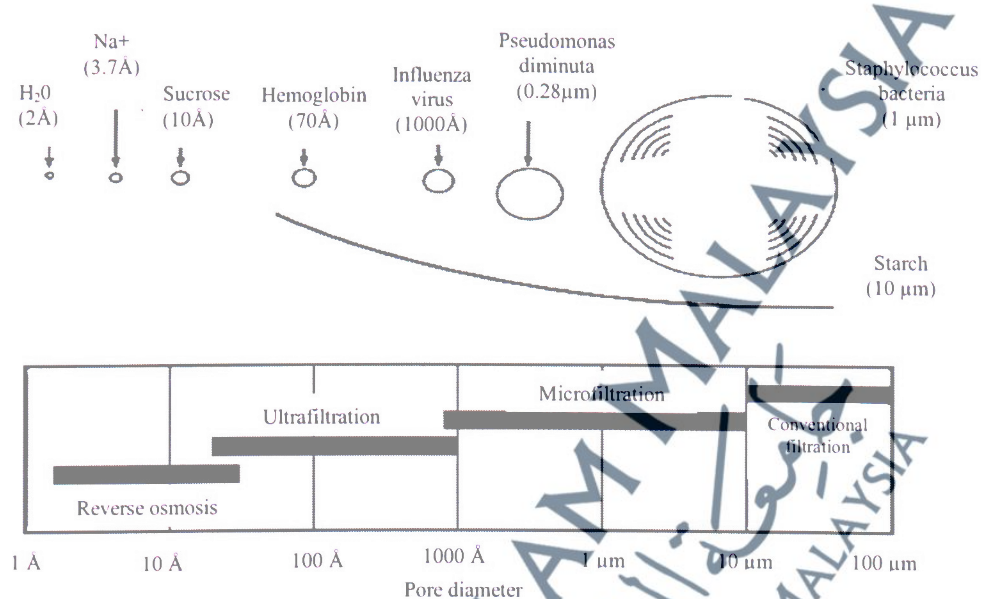
INTRODUCTION

1.1 Membrane Process: Ultrafiltration

Membrane processes have been widely used in industries. It can be classified into different categories based on driving force used for filtration. Just as, driven membrane filtration process has three types in which concentration, electrode potential difference and pressure. The concentration driven membrane filtration is called dialysis process while the electrode potential difference filtration is known as electrodialysis. There are four pressure driven membrane filtration processes which are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) (Nielsen, 2000; Cheryan, 1998). These industrial membrane separation processes are all well established.

All these processes were differing principally in the average pore diameter of the membrane. The range of application of this pressure-driven membrane separation process is illustrated in Figure 1. In this study, UF is more focused compared to the other processes. Due to the different pressure driven, the processes can be classified on the basis of the size of the molecules or components passing through the membrane filtration process (Mistry, 2002).

FIGURE 1: The Relative Size of Different Solutes Removed by Each Class of Membrane



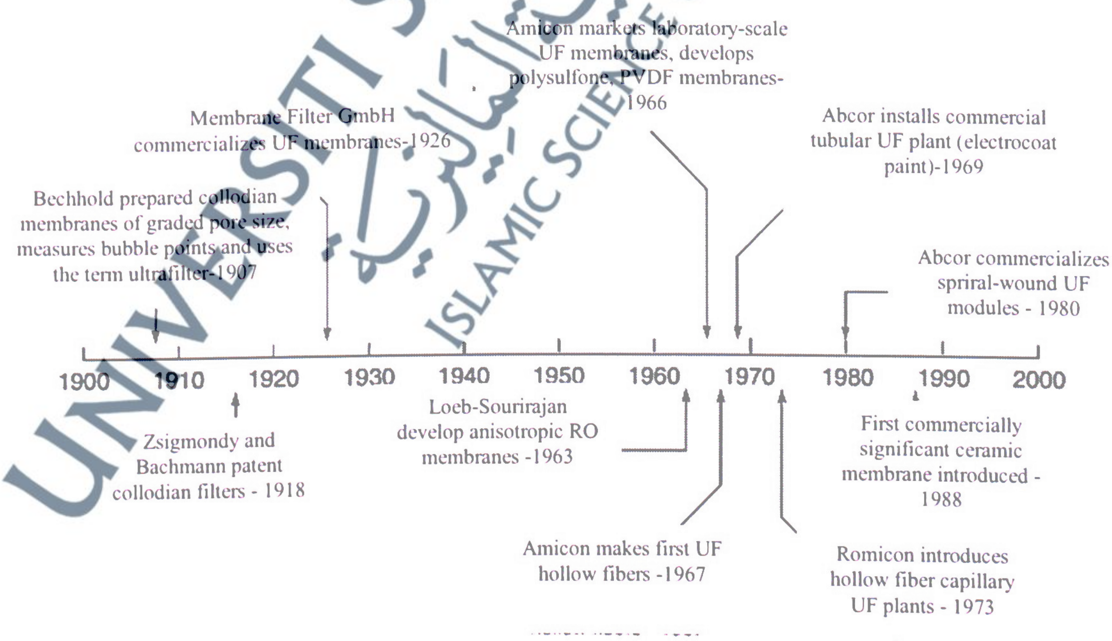
Source: Baker, 2004

UF uses a finely porous membrane to separate water and microsolutes from macromolecules and colloids. The average pore diameter of the membrane is in the 10-1000Å range. The first synthetic UF membranes were prepared by Bechhold from collodion (nitro cellulose). He was probably the first to measure membrane bubble points, and he also coined the term ‘ultrafilter’. Collodion UF and MF membranes were commercially available for laboratory use by the mid-1920s. However, no industrial applications existed until 1960s although collodion membranes were widely used in laboratory studies. In 1696, Abcor installed the first commercially successful industrial UF system equipped with tubular membrane modules to recover electrocoat paint from automobile paint shop rinse water (Baker, 2004).

The first cheese whey UF system was installed shortly thereafter 1970. In addition, 100 similar systems had been sold worldwide within a decade. These early system used tubular or plate-and-frame modules, which were relatively expensive therefore lower cost designs were gradually introduced. In 1973, Romicon was first sold hollow fiber (capillary) modules then, spiral-wound modules adapted to UF applications by Abcor. Both were became commercial items by 1979-1980. The UF industry has grown steadily over the last 20 years.

Recently, ceramic-based UF has been developed by several companies. These membranes have found a place in applications that require resistance to high temperatures or require regular cleaning with harsh solutions to control membrane fouling. Some of the milestones in the development of UF membranes are shows in Figure 2 (Baker, 2004).

FIGURE 2: Milestones in the Development of Ultrafiltration



Source: Baker, 2004

1.2 Membrane Materials

One of the factors that contribute to the successful fabrication of a high-performance membrane is membrane materials itself. Membrane materials with the appropriate chemical, mechanical and permeation properties must be selected because this choice is very process-specific. Once the membrane material has been selected, the technology required to fabricate this material either into a robust, thin or defect-free membrane. After that, the membrane has been packaged into an efficient, economical, high-surface-area module is similar for all membrane processes. Membrane materials can be divided into two types which are organic membrane and inorganic membrane. Typical materials used in formulating organic membranes are:

- Polyethylene (PE)
- Polytetraflouroethylene (PTFE)
- Polypropylene (PP)
- Cellulose acetate (CA)
- Polyacrylonitrile (PAN)
- Polyimide (PI)
- Polysulfone (PSf)
- Polyethersulfone (PES)
- Polyvinylidene difluoride (PVDF)

On the other hands, the primary materials used for inorganic membranes are:

- Aluminium oxide (Al_2O_3)
- Zirconium oxide (ZrO_2)

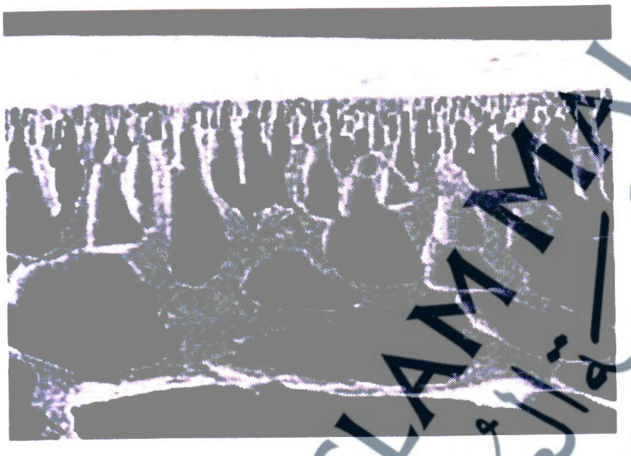
In addition, glass (Sirasu Porous Glass) and stainless steel also has been tried to be used as membrane materials. Inorganic membranes can be excelled in chemical resistance as well as in the mechanical strength and heat properties. The production of inorganic membrane materials will give in highly cost because of these advantages. Currently, both organic and inorganic materials have been used to manufacture membranes (Mulder, 1991; Cheryan, 1998). Besides, there are two classes of organic membrane materials which are hydrophobic materials and hydrophilic materials (Zeman and Zydney, 1996).

Most of today's UF membranes are made by limited number of materials primarily polyacrylonitrile, poly (vinyl chloride)-polyacrylonitrile copolymers, polysulfone, poly (ether sulfoen), poly (vinylidene fluoride), some aromatic polyamides and cellulose acetate. In general, the more hydrophilic membranes are more fouling-resistant than the completely hydrophobic materials. Water-soluble polymers such as poly (vinyl pyrrolidone) or poly (vinyl methyl ether) are often added to the membrane casting solutions used for hydrophobic polymers such as polysulfone or poly (vinylidene fluoride) (Baker, 2004).

1.3 Asymmetric Membrane Formation

The structure of a membrane is vital for its performance for it dictates the separation and permeation mechanism. There are two types of membrane structures may be distinguished which are symmetric and asymmetric membranes. The membranes are either symmetrical, where the properties of the membrane do not change throughout the cross-section of the membrane or are asymmetrical, in which case the membrane is composed of a thin selective layer and a strong supportive layer giving mechanical strength as shown in Figure 3.

FIGURE 3: Asymmetric Membrane Structure



Source: Fontananova et al., 2006

Asymmetric (anisotropic) membrane has different chemical and/or has different chemical and/or physical structures in the direction of its thickness. It is typically characterized by a thin "skin" on the membrane surface with small pore size and a thickness of 0.1 to 0.5 μm. This dense layer is supported by a porous structure with larger pore size and a thickness of 50 to 150 μm. Besides, asymmetric membranes are in general superior compared to symmetric membranes because the flux determining top layer can be very thin. Due to this unique ultrastructure, rejection only occurs at the surface and retained particles do not enter the main body of the membrane. Asymmetric membranes offer great possibilities in optimizing the membrane separation properties by varying the preparation parameters of the thin top layer in particular (Kang et al., 1991).

Polymer asymmetric membrane can be prepared using phase inversion methods in which both the selective layer and the supportive layer can be formed in one single preparation step. The ongoing development of polymeric asymmetric membrane throughout the decades resulted in the use of polymers like polysulphone (1965), polyether-ether-ketone (1980) and polyetherimide (1982). This phase inversion process was involved the phase separation of a homogeneous polymer solution into two phases which are polymer-rich phase and polymer-poor phase. The former resulted in a rigid, structural form of the membrane while the latter gave a porous structure. Moreover, the phase separation process determines the membrane morphology which in turn governs the transport characteristics of the resulting membranes (Kang et.al., 1991).

1.4 Research Background

A common technique for preparation of polymeric membranes with the asymmetric structure is the phase inversion where a thin layer of the polymer dissolved in an appropriate solvent is cast on a suitable support and phase separation is introduced by a non-solvent (Madaeni et al., 2005). Most studies of phase inversion mechanism, ultra-thin skin layer formation, membrane morphology and pore size control were based on flat sheet or single layer asymmetric membranes (Jiang et al., 2004). Asymmetric membrane is characterized by a thin and dense skin layer on top of a porous substructure. Its capability is to reject or admit a certain solute species, therefore, determined by the morphology, pores properties and dense degree of the skin layer (Chuang et al., 2000). Low molecular weight component or the secondary material is frequently used as additives in the forming system in order to control the membrane pores and structures, because it offers a convenient and effective way to develop high performance membranes (Kesting, 1985).

Membrane morphology and ultimate permeation properties depend on many variables. For membranes prepared by the wet phase inversion method, the key parameters are: the chosen polymers-solvent-non-solvent system and their compositions, the thermal history of the membrane casting solution, the non-solvent conditions, evaporation conditions and the process variables (Pezeshk et al., 2012). Recently, UF membranes have been successfully prepared by phase-inversion method using poly(phthalazinone ether amide) (PPEA) as membrane material and thus the membranes have shown good separation properties (Wu et al., 2008).

Some researchers studied the effect of natural additives such as maleic acid and piperazine on performance of polyethersulfone (PES) UF membrane (Chaturvedi et al., 2001). The influences of the addition of inorganic salts and the surface tension on the membrane formation are reported by Kraus et al. (1979). In addition, water, inorganic salts, low molecular weight organics, polymers, mineral fillers or a mixture of them were found to affect the final membranes properties. Ping et al. studied the mechanism of addition of organics in the polysulfone (PSF) membrane casting solution. The presence of an additive is one of the factors that affect the membrane structure and performance (Ping et al., 1991). Kim and Lee investigated the effect of PEG additive as a pore-former on the structure formation of PSF membranes (Kim and Lee, 1998).

The effects of surfactants on the polymeric membranes were studied by many researchers. Sodium dodecyl sulphate (SDS) was used as a surfactant additive in PSF casting solution for gas separation and as s gelation media in formation of PES membranes (Yamasaki et al., 2000; Alsari et al., 2001). Tsai et al (2000) reported that Span 80 can restrain the macrovoid formation and improve the prevaporation performance of PSF membranes. Besides, it was found that increasing the Tetronic 1307 surfactant concentration will increase the membranes hydrophilicity (Rahman et al., 2008). Also it was reported that Tween 80 increase water content and porosity of the membrane support layer and also enhances pure water permeability (Amirilargani et al., 2010). Increasing the Tween 80 also give effect for PES ultrafiltration membranes which decreases the rejection ratio of bovine serum albumin, increase the flux recovery ratio and decrease the degree of irreversible fouling (Amirilargani et al., 2009).

Most of the researches were commonly focused on the effect of surfactant towards performance and physical characteristics of the membranes. Hence, in this research will covers on the roles of surfactants on membranes pores characteristics which controlling pores towards pore properties (pore size, pore length, pore width) and pore structures (pore types, pore dense, macrovoid-microvoids pores and its morphologies) of asymmetric UF membranes.

1.5 Problem Statement

As a membrane material, poly(vinylidene fluoride) (PVDF) is a polymer that normally used in the making of asymmetric membrane. It is soluble in high-boiling point solvents and high hydrophobicity which make it easier to fabricate more permeable asymmetric membranes by phase inversion via immersion precipitation method. The presence of additive is one of the factors that affect membrane structure and performance thus increases the hydrophilicity of the membranes. Nevertheless, this common phase inversion induced by immersion precipitation technique is not versatile enough to prepare the appropriate membrane structure and properties. Hence, suitable materials need to be introduced in the casting solutions in order to prepare membranes with good penetration properties.

The secondary addition of new materials such as surfactant is one of the effective strategies to produce membranes with optimal and specific properties. Several studies on the effects of surfactants on the polymeric membranes discovered that the surfactant is significant for the improvement of membranes hydrophilicity, water flux and separation performance. However, there is no fundamental study reporting on the roles of surfactants on membrane pores and its characteristics. As one of the key properties which are strongly determining the membranes performance and properties, research on the important and effectiveness of surfactant towards the controlling of membrane pores and pores structures in newly polymeric ultrafiltration membranes are very essential and fundamentally important.

Moreover, the important data on pores sizes, pores properties and pores structures are very essential in the aspect of membranes pores characterization which thus commence towards the critical knowledge on the performance-properties-morphologies of the first ultrafiltration-surfactants membranes. Therefore, towards producing of fine and narrow pores of UF membrane, the key roles of surfactant materials on the pores, pore properties and pore structures are to be discussed. In this study, the effect of surfactant in terms of types of additives (primary), surfactant types and surfactant concentration towards the preparation of newly polymer-surfactant UF membrane will be determined. This pioneering work will integrate the science bridging polymer-surfactant fundamental knowledge on membrane making and performance-properties-pores of asymmetric ultrafiltration membranes. Thus, this study is very important in the aspect of novelty and will benefit to the establishment of membranes development and its industrial applications in the future.

1.6 Objectives of the Study

The main objectives of this research include:

a) To formulate of a newly polymer/solvent/additive/ surfactant dopes component system.

b) To prepare a newly narrow-pores ultrafiltration (UF) membrane based dry/wet phase inversion technique.

c) To determine the effects of surfactant on the water flux, permeability, separation factor and key properties of UF membranes.

d) To investigate the major roles of surfactant on the morphologies, membrane pores and pore properties of polymeric UF-Surfactant (UFS) membranes.

1.7 Scopes of the Study

From this study, we will be able to:

a) Formulating of polymer/solvent/additive/surfactant dopes component system.

b) Developing the newly narrow-pores ultrafiltration (UF) membranes based dry/wet phase inversion technique.

c) Determining the effects of surfactant on the water flux, permeability, separation factor and key properties of UF membranes.

d) Investigating the major roles of surfactant on the membrane pores and pore structures of polymeric UF membranes.

e) Characterizing of membranes pores (pore size, pore length and pore width) and structural details (pore types and sub-layer structures) via SEM approach.