Preparation, Characterization and performance optimization of Ultrafiltration membranes produced with polymeric and inorganic additives

A Major Qualifying Project Report

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Anil Saddat

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Professor David Dibiasio, Advisor

Abstract

As the industrial demand for increasingly effective ultrafiltration (UF) membranes rises, the creation of optimized membranes has risen to the forefront of laboratory research. This project studies the cause and effect relationship between combinations of UF membrane design variables and their corresponding performance responses. Using uniform experimental design and linear regression techniques it was possible to produce membranes with superior functionality. It was found that doping of PVC/PVB with PEG-600 or PVP could produce a membrane with increased rejection and water flux values which allows for industrial scale applications.

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Executive summary:

UF membranes are a critical part of the chemical industry. They are used mainly for the physical separation of particles, as they have the ability to segregate these particles based on their size. In recent years the application base for UF membranes has increased drastically, ranging from pharmaceuticals to water purification. This immense demand drives researchers to continuously try and produce more cost effective membranes with increased performance values. The efficiency of these membranes depends on a range of variables which control their ultimate performance. This experiment focused on controlling these variables and studying the performance of produced membranes in order to evaluate a cause and effect relationship. This relationship was in turn used with regression techniques for the development of membranes with superior functionality.

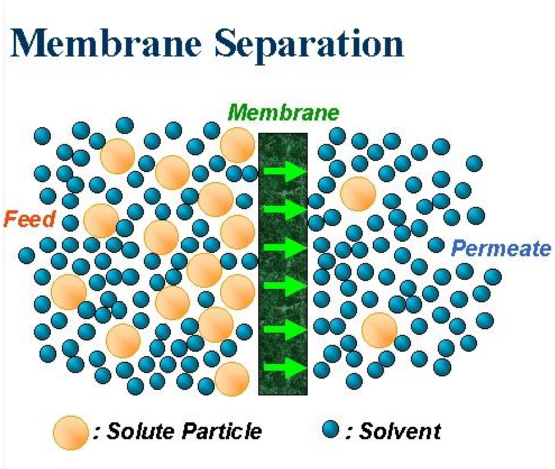


Figure 1: Membrane separation technology: (20: Google images Conc-Polarization)

In the present work, the effect of doping polyvinyl chloride (PVC)/ polyvinyl butaral (PVB) blend flat sheet membranes with different additives on the ultrafiltration performance was investigated. These additives include calcium nitrate, lithium chloride, poly-vinyl pyrrolidone (PVP), and polyethylene glycol 600 & 100 (PEG 600 & 1000). In order to conduct the experiment efficiently and optimize membrane functionality, Taguchi's uniform experimental design method was used. PVC/PVB blend ratios, weight percentage of the total amount of polymer, additive type, the weight percentage of the additive, and water bath temperature were all the controlled variables. These variables were combined in different amounts according to the experimental design method to produce ten different kinds of membranes. These combinations are illustrated below:

Table 1: The final set of design combination used to create the different membranes.

Experiment	Temperature of bath (A)	PVC/PVB (Blend Ratio)(B)	Wt.% of Polymer(C)	Additive (D)	Wt. % of Additive. (E)
1	40	9:1	20	PVP	7
2	40	8:2	18	LiCl	3
3	50	7:3	10	PEG 1000	10
4	50	6:4	21	LiCl	5
5	60	5:5	20	PEG 1000	1
6	60	9:1	15	CaNO3	10
7	70	8:2	10	PEG 600	5
8	70	7:3	21	CaNO3	1
9	80	6:4	18	PEG 600	7
10	80	5:5	15	PVP	3

The produced membranes were tested with scanning electron microscopy, atomic force microscopy; Fourier transformed infrared spectroscopy, viscometers and CA goniometers. These tests were run in order to characterize the membranes according to their morphology, surface terrain, bulk functional groups, viscosity and contact angle. The performance evaluations were represented using porosity, pure water flux and retention of protein particles through the membranes. The main performance responses of the membranes are shown below:

Table 2: Performance of membranes

EXP #	Flux (L/m^2.hr)	Rejection (%)
1	443.808	6.81
2	89.1	52.12
3	2164.32	9.3
4	5388.66	0.83
5	4026.708	5.08
6	1203.12	8.59
7	534.672	30.45
8	142.38	72.57
9	214.776	70.35
10	889.272	34.31

The combination of design variables which make up the different membranes (Table 1) and their corresponding performance responses (Table 2) are used with linear regression in order to predict variable combinations which give optimum performance values. According to the regression performed the following combinations are predicted to give the following optimized performances.

Table 3: Combination for producing optimized membranes

Additive	Weight % Additive	Bath Temperature	Blend Ratio	Flux(L/m^2.hr)	Rejection
PEG 1000, LiCl	1	40	90	1210.028	26.13
PEG 600, LiCl	1	80	80	330.408	66.24
PVP,Ca(NO3)2	1	100	10	3614.448	34.49
PEG 600, PVP	10	50	100	187.608	83.98675

From the table above it can be seen that a membrane with a PEG-600, PVP/PVC/PVB construct will be able to reject 84% of 20000 Da proteins with a flux of 188 liters/m^2.hr. This is a good balance between flux and rejection and should be sought for more effective industrial applications.

Introduction

Membranes are used widely in the chemical industry to separate solute molecules such as proteins on the basis of size. Ultrafiltration (UF) membranes are used to separate molecules around particle sizes of 10^{-3} to 10^{-6} Da*. UF membranes differ from other particle separators because it has an anisotropic structure; which essentially means that it has a thin layer with small pores that improves the selectivity while the mechanical support is provided by a much thicker highly porous layer. UF membranes are used widely in the pharmaceutical, chemical and food industries to separate vaccines, fermentation products, enzymes and other types of proteins. [1]

Producers for UF equipment are constantly looking for new polymers to create inexpensive membranes. These membranes are required to have a balance between the cost of production and adequate mechanical strength and thermal/chemical resistance, ease of preparation and most importantly be efficient and selective. Poly-vinyl chloride (PVC) is a compositive resin with the benefits of abrasive resistance, acid and alkali resistance, microbial corrosion resistance and chemical performance stabilization. PVC is commonly used to produce relatively inexpensive UF membranes. Further study has been conducted to show that blending of PVC with other more hydrophilic polymers like poly-vinyl butaral (PVB) can improve the balance between membrane performance and cost of production. [2]

It is also known from previously conducted studies that additives like lithium chloride (LiCl), poly-vinyl pyrrolidone (PVP) and poly-ethylene glycol (PEG-600, PEG 1000) could further improve the performance of UF membranes. These studies focused on the performance variations due to a change in the amount of additive or a change in the amount of polymer. But these changes in performance can also be used with statistical analysis to evaluate a UF membrane which shows an optimum balance between efficiency and selectivity.

The purpose of this research was to evaluate and analyze a group of membranes prepared from PVC, PVB and different blends of additives. This analysis helps to determine an optimum PVC/PVB blend and the additive which shows the largest performance improvement. Hence these evaluations can be used with theories of experimental design to predict a membrane with optimum functioning performance.

Background

Ultrafiltration Membrane:

Membrane filtration is a simple mechanism which uses a certain driving force (e.g. hydrostatic pressure) against a semi-permeable material to separate materials as a function of their physical and chemical properties like size and intermolecular forces.[i] In membrane separation processes, the feed is separated into a stream that goes through the membrane, *i.e.,* the permeate and a fraction of feed that does not go through the membrane, *i.e.,* the retentate or the concentrate. A membrane process then allows selective and controlled transfer of one species from one bulk phase to another bulk phase separated by the membrane.[3]

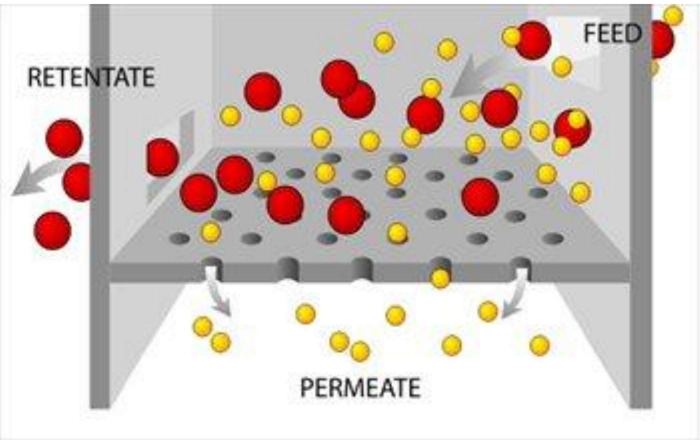


Figure 2: Basic membrane filtration mechanism. **20: www.nanoglowa.com**

The type of membrane and the process of separation is based on its nature, structure and/or driving force. Microfiltration (MF), nanofiltration (NF), reverse osmosis (RO) and gas separation (GS) use hydrostatic pressure differences as a driving force for the transport of selective particles through the membrane. Ultrafiltration (UF) is also one of the membrane processes which use pressure difference as its driving force. Ultrafiltration in its ideal definition is a separation technique that can simultaneously concentrate macromolecules or colloidal substances in the process stream. Ultrafiltration can be considered as a method for concurrently purifying, concentrating, and fractionating macromolecules or fine colloidal suspensions.

Ultrafiltration membranes serve as a molecular sieve for particle separation. The basic difference between Ultrafiltration membranes and its counterparts is the size of particles that it separates. Ultrafiltration membranes works on particles in the range of 1000 to 500000 Da (where 1 Da is $1.660\,538\,78 \times 10^{-27}$ Kg).

Another distinguishing feature is the asymmetric anisotropic structure of the membrane. In an anisotropic membrane a thin layer with small pores is formed over a thicker highly porous layer. The thin layer provides for the membranes selectivity and the thick porous layer acts as the mechanical support.

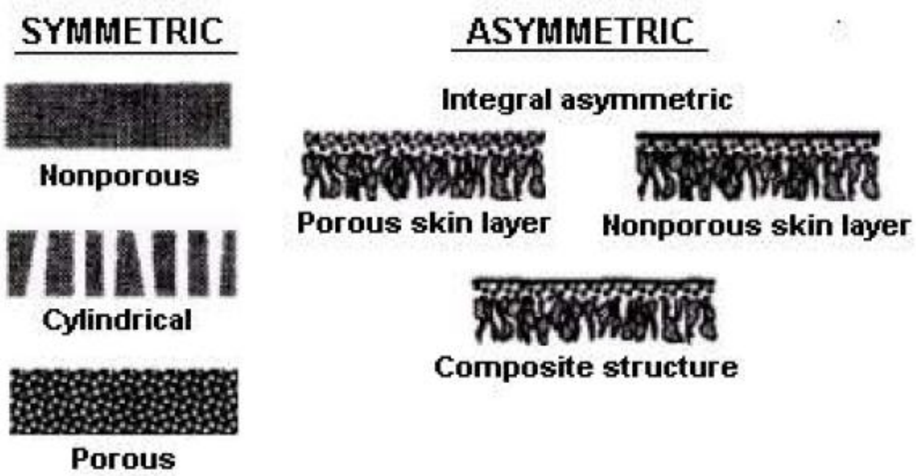


Figure 3: Schematic representation of symmetric and asymmetric membrane cross-section [22: Strathmann, 2001]

Transport Mechanism

One of the most important aspects of determining the performance of an ultrafiltration system is the rate of solute or particle transport towards the membrane. This is measured in volume per unit area per unit time. As shown in Fig. 2, the pressure difference across the membrane feed and the retentate and permeate side forces the solution particles towards the upstream surface of the membrane. If the membrane is partly, or completely, selective to a given solute, the initial rate of the particle transport toward the membrane, J.C, will be greater than the solute flux through the membrane, $J.C_p$. This causes the retained particles to deposit at the surface of the membrane. This is generally referred to as concentration polarization, a reversible mechanism that depends directly on the pressure difference driving the process. The solute concentration of the feed solution adjacent to the membrane varies from the value at the membrane surface, C_w, to that in bulk solution, C_b, over a distance equal to the concentration boundary layer thickness, δ. The buildup of retentate at the surface of the membrane leads to the particles diffusing back towards the bulk of the solution, $-De.\frac{dC}{dX}$. Steady state is reached when the rate of particle flow towards the membrane is equal to the flux through the membrane in addition to the rate of diffusive back transport of the particles to the bulk solution. i.e.:

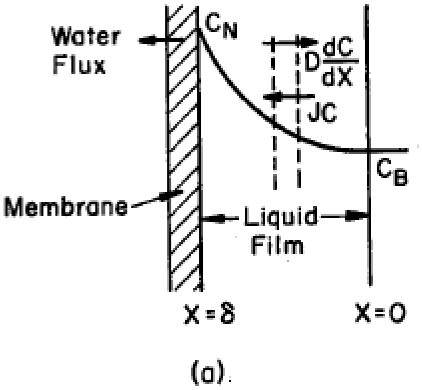


Figure 5: Solute transfer without layer formation (1: Schuler & Kargi)

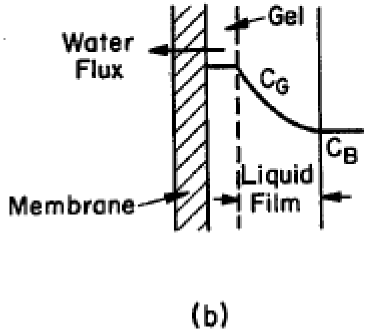


Figure 4: Solute transfer with gel formation (1: Schuler & Kargi)

$$J.C = De.\frac{dC}{dX} + J.Cp$$

Where, De = effective diffusivity of the solute in liquid film (cm^2/s)

J = volumetric filtration flux ($cm^3/cm^2.s$)

C = concentration of the solute (mol/cm^3)

Cp = concentration of the permeate (mol/cm^3)

C_G = maximum value of C_w (mol/cm^3)

X = film thickness (cm)

Separating the variables and integrating the above equation gives:

$$\ln\frac{Cw - Cp}{Cb - Cp} = \frac{J\delta}{De}$$

Where, Cb = Concentration of the bulk solution (mol/cm^3)

Cw = concentration of the solute particles at the membrane surface (mol/cm^3)

The ratio of the diffusivity coefficient of De and the thickness of the boundary layer can be written as k, which is the mass transfer coefficient. The equation can be written as follows:

$$J = k.\ln\frac{Cw - Cp}{Cb - Cp}$$

For a flux limiting situation when all the solutes are completely retained Cp = 0 hence the equation transforms to:

$$J = k.\ln\frac{Cw}{Cb}$$

The concentration at the surface of the membrane C_w can be found by extrapolating the curve which is obtained by plotting J versus Cb.

The amassing of particles at the membrane surface can affect the permeate flux in two different ways. Firstly, the accumulated solute can initiate an osmotically driven fluid flow in the opposite direction of the permeate flux, thereby reducing the net rate of solvent transport. This phenomenon is often more prominent for smaller solute particles because of the high osmotic pressure (*e.g.*, retained salts in reverse osmosis). Secondly the can be intense amounts of membrane fouling due to chemical and physical interactions between the particles in the process stream and the components that make up the membrane, thereby providing an additional hydraulic resistance to the solvent flow in series with that provided by the membrane. These interactions can be attributed to adsorption, gel layer formation and plugging of the membrane pores.

Applications of Ultrafiltration membranes:

Ultrafiltration membranes are being used increasingly in the food, beverage, pharmaceutical and chemical industry. One of the most important uses of ultrafiltration membranes is that of wastewater treatment. Today, UF technology is being used worldwide for treating various water sources.

The reasons for the increased use of ultrafiltration membranes in the water purification industry can be attributed as follows increased regulatory pressure to provide better treatment for water, increased demand for water requiring exploitation of water resources of lower quality than those relied upon previously, and market forces surrounding the development and commercialization of the membrane technologies as well as the water industries themselves.[3]

The use of UF technology for municipal drinking water applications is a relatively recent concept, although as mentioned before, it is commonly used in many industrial applications such as food or pharmaceutical industries.[3]

Electro-coat paint and Ultrafiltration:

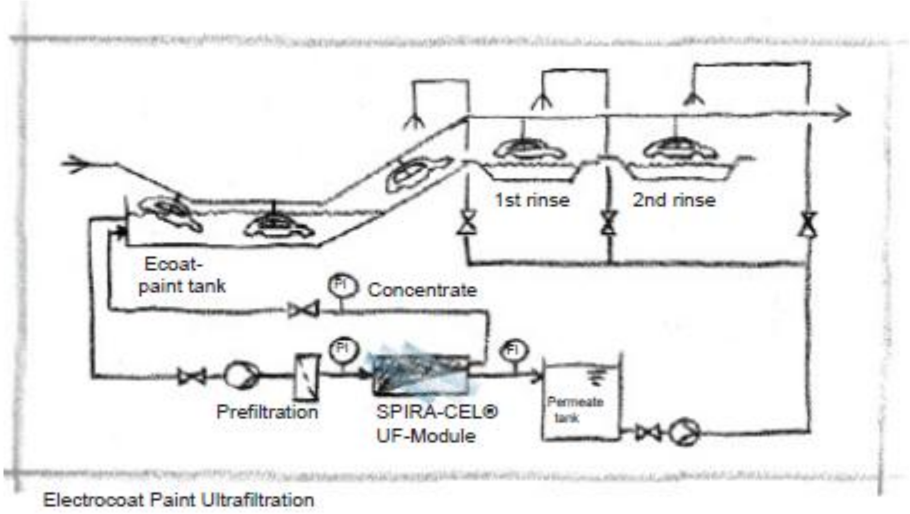


Figure 6: Electro coat paint & ultrafiltration (23: Munir, UF and MF handbook)

Electrophoretic coating gives a homogeneous and defect free coat. This process involves the electrophoretic deposition of charged paint particles in an aqueous solution onto a conductive (metal) work piece. While the permeate from the ultrafiltration module is used for rinsing the work pieces, there is a stream that takes the mixture of water and paint back to the e-coat paint tank. The introduction of an ultrafiltration unit helps to eliminate the production of waste water and the use of extra de-ionized water for rinsing

Food industry and Ultrafiltration:

Ultrafiltration is found in various sectors in the food industry, especially companies that produce milk, gelatinous food products and large scale meat processing.

Meat Processing:

Figure 7: New Ultrafiltration water treatment concept for the meat processing industry. (18: Huber)

Around 90% of the water used for meat processing is discharged as waste water. This water has significant amounts of organic matter, high levels of COD and BOD_5, high concentration of etheric extract, suspension, biogenic and dissolved substances. Ultrafiltration is used to remove colloids, suspended and macromolecular matter. [18]

Gelatin Production:

In the past gelatin was extracted in solution by alternately soaking and cooking animal hides in up to 8-10 runs, filtering the solution and passing it through an ion exchanger to remove the salt which is a natural by-product of gelatin production. Water is removed from the solution by evaporation and drying. With the use of evaporators and driers a total solid content of 90-92% was possible. And this evaporation and drying process took up 45% of the total energy required for the gelatin production process.

Using spirally wound UF membrane units, 90% of the water content can be removed, and with the help of lower number of evaporators and driers a solid content close to 98% can be reached. With the new UF membrane system there is less degradation of the protein molecule so there is a higher product quality, the amount of natural gas or oil required decreases by a lot for which carbon emissions decreases and also the amount of water required from outside sources decreases. There are a number of other benefits most importantly lower operating costs, increased control because individual units can be run for required product outputs, reduced labor because of lower maintenance and easier cleaning methods. The amount of electrical power also decreases while a larger amount of steam can be conserved. [4]

Figure 8: A spirally wound UF membrane system (24: trade gateway)

Miscellaneous Applications:

Ultrafiltration of oil-water emulsions:

Oil water emulsions are commonly used as metal working fluids (MWF) in different kinds of machining and rolling processes to lubricate and cool the work piece, remove chips out of the cutting zone and most importantly to prevent corrosion. These emulsions consist of a complex mixture of water, oil and additives such as emulsifiers, corrosion-inhibitors, antifoaming and extreme pressure agents. These MWF must be replaced over time because of the severe working conditions and the contaminants they collect. The dumping of this oily wastewater poses as a severe environmental threat.

Several methods exist to treat MWF wastewater such as oil skimmers, centrifuges, and coalescers, settling tanks, depth filters, magnetic separations and flotation technologies. But owing to the size of the particles Ultrafiltration is a very successful treatment system but there because of the high quality of permeates that is attained.[5]

Ultrafiltration in Pulp and paper processing:

The pulp and paper industry is challenged by the water authorities to bring substantial reduction in their ejection of toxic pollutants or face legal reprisal. The effluents produced during the manufacturing of paper contain biologically inactive substances that can be harmful for the environment. Not only are these substances toxic by nature, but they also possess light-absorbing characteristics that influence the light-penetration properties of water, thereby, causing death to most water based organisms.

The wastewater originating from pulp and paper processing can be treated using various methods. These include aerobic and anaerobic treatments, lime and alum coagulation and precipitation, oxidation, adsorption onto ion-exchange resins and most importantly Ultrafiltration.

Treatment of pulp and paper effluent by means of UF is an efficient method, as most of the polluting substances consist of high molecular mass compounds that are easily retained by UF. UF treatment of the effluent can result in 70–98% removal of color, 55–87% removal of chemical oxygen demand (COD) and 35–44% reduction in biological oxygen demand (BOD).[6]

PVC and PVB based Ultrafiltration membranes:

As mentioned before there is extensive research being conducted on novelty materials that can possibly improve the balance of performance characteristics of Ultrafiltration membranes. Some of the commonly used polymers for the production of UF membranes are polysulfone (PS), polyetherimide, (PEI), polyvinylidenefluoride (PVDF), and cellulose triacetate (CTA). One of the more common relatively inexpensive membrane materials is polyvinyl chloride (PVC) which provides for good chemical and corrosion resistance.

The solubility parameter is an important indication of polymeric characteristic. It is a function of cohesive density which consists of dispersion forces, dipole forces and hydrogen bonding forces. That is:

$$\delta sp = \sqrt{\frac{\Delta E}{V}}$$

$$\frac{\Delta E}{V} = \frac{\Delta Ed}{V} + \frac{\Delta Ep}{V} + \frac{\Delta Eh}{V}$$

Hence, $\delta sp^2 = \delta d^2 + \delta p^2 + \delta h^2$

Here the right hand side of the equation is characterized by the dispersion, dipole and hydrogen bonding forces. The solubility parameter of PVC, δsp, PVC is 9.5 $(cal/cm^3)^{1/2}$; δ*d* and δ*h* of PVC are respectively 1.45 and 8.65 $(cal/cm^3)^{1/2}$, which demonstrates low hydrogen bond, intermolecular force and poor hydrophilics.[2]

One more concern while designing an UF membrane is the fouling factor. Fouling occurs when membrane pores are blocked by particles being filtered. This may cause decrease in the flow rate of liquid (Flux) through the membrane. The best way to decrease this effect is to blend the membrane with more hydrophilic polymers.

The performance of a certain material can be improved by blending the original base polymer with other polymers with more adequate properties. However the main obstacle in doing so is that not all polymer pairs are readily miscible. The miscibility of polymer occurs in three situations: low molecular weights (negligible entropy of mixing), chemically similar polymers (relatively low unfavorable heat of mixing), and polymers that show specific interactions between the molecules (highly favorable heat of mixing). Another important factor that should be taken into account is the interactive forces between the particles being transported and the polymer component of the membrane. Since ultrafiltration common deals with water molecules the amount of hydrophilicity (likeness towards water) counts for a lot. PVC membranes are relatively less hydrophilic; therefore blending with a more hydrophilic component is important for process improvement and increased efficiency.

Polyvinylbutaral is a hydrophilic polymer and has the following structure:

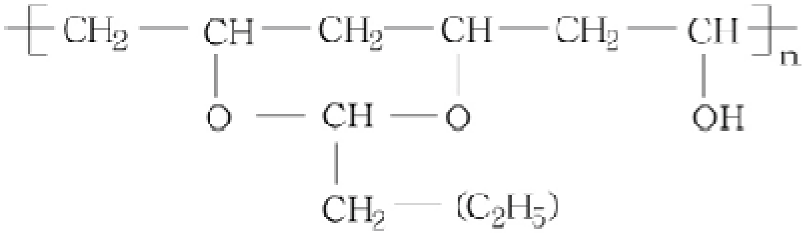


Figure 9: -OH bond makes the PVB polymer more hydrophilic.

As shown in the above figure the PVB monomer has a hydrophilic hydroxyl group. Owing to this the solubility parameter of PVB is δsp = 8.76 $(Cal/cm^3)^{1/2}$ hence PVB can be blended with PVC to improve hydrophilicity of PVC based UF membranes. PVC and PVB are also compatible because of their well predicted miscible properties, chemical similarity and a small unfavorable heat of mixing.[2] Most importantly owing to the –OH bond, the PVC/PVB blend is predicted to be much more hydrophilic than the original PVC membrane.

Solvent:

Dimethylacetamide is the organic compound with the formula $CH_3C\ (O)\ N\ (CH_3)_2$. This colorless, water miscible, high boiling liquid is commonly used as a polar solvent in organic chemistry. DMAc is miscible with most other solvents, although it is poorly soluble in aliphatic hydrocarbons.

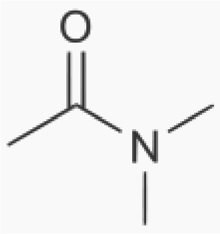


Figure 10: N-N Dimethylacetamide
25: wikipedia

DMAc was chosen for the purpose of this experiment because of expected trends observed from other studies on the interaction of PVC and DMAc. The relative viscosity is fairly low and balanced in DMAc casting solutions. The interaction with PVC isn't too high to produce a non-fluid casting solution but then again the solution won't be too runny for it to produce a weak membrane. The same goes for the crystallinity of the casting solution where the amount of crystals formed is fairly low for DMAc casting solutions. Also another notable advantage is that the relative viscosity and crystallinity does not change drastically with the addition of other components.[7]

Additives:

Additives are used alongside PVC/PVB to further increase membrane performance. Generally, additives create a spongy membrane structure by prevention of macro voids formation, enhance pore formation, improve pore interconnectivity and introduce further hydrophilicity. The main additives that were tested during this research were poly ethylene glycol (PEG) -600, 1000, poly-vinyl pyrrolidone (PVP), lithium chloride (LiCl) and also calcium nitrate ($CaNO_3$). [8]

PEG – 600, 1000:

Poly ethylene glycol or PEG is a poly ether compound which is commonly used in the manufacturing and pharmaceutical industry. PEG as additive is less frequently used compared to PVP, but it could play a similar role in the formation process, acting as a macro void suppressor and improving the membranes hydrophilic characteristics. (Ma et al 2010) The numbers that follow PEG represents the average molecular weight and the monomer is illustrated below in figure 8. Molecular weights of PEG range from 100 to 500,000 Da but for this experiment the lower molecular weights are used because of their higher, favorable heat of mixing.

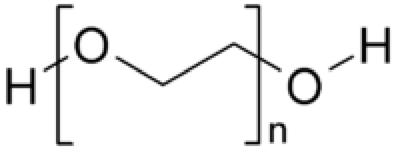


Figure 11: Molecular structure of PEG
(26 Wikipedia)

In studies conducted before many conclusions were drawn on the effect of using PEG as an additive for UF membranes. PEG is known for increasing porosity/permeability and thermal/chemical stability of the membrane. PEG, being hydrophilic in nature, can also be used to improve membrane selectivity as well as a pore forming agent. It was also seen that with an increase in molecular weight of PEG, the pore number as well as pore area in membranes increases. Membrane with PEG of higher molecular weight has higher pure water flux (PWF) and higher hydraulic permeability due to high porosity. More specific studies showed that the addition of PEG-600 is expected to increase the exchange rate of additive and non-solvent during the membrane formation process, resulting in the appearance of the macro voids formation while hydraulic permeability decreases. [10]

All these studies have been conducted on different kinds of polymeric materials but interaction of PEG with PVC is not well documented. Hence learning the effect of PEG on PVC blended membranes is important to see if the it follows the expected trend.

PVP:

Polyvinyl pyrrolidone (PVP) also known as polyvidone is a water soluble polymer. The single PVP monomer is illustrated below:

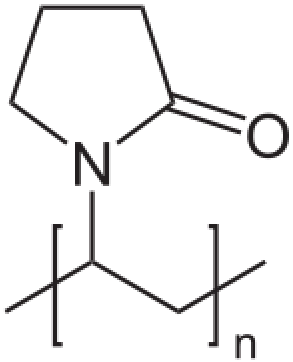


Figure 12: Monomer of PVP
(27: Wikipedia)

The N-C=O bond makes PVP extremely hydrophilic and its addition to the membrane could improve the permeability of the membrane. As a resulted the fouling rate is also expected to decrease. There is one known disadvantage in using PVP; it is expected that the flux of solution through the membrane will decrease because PVP swells to decrease the size of the pores. [11]

From previous studies that were conducted the general trend of PVP doping shows the following changes to membrane characteristics.

1. An increase in the pore density
2. The thickness of the more selective porous layer decreases due to an increase in the amount of macro voids in the support layer.
3. An increase in the hydrophilicity for the bulk of the membrane.

PVP is a very commonly used additive and generally helps improve the performance of the membrane. The blend of PVC/PVB/PVP should produce an interesting membrane to study. [12]

Inorganic Additives:

Inorganic Salts like lithium chloride and calcium nitrate is known to develop membrane morphologies and performance. And these additives are also known to change the solvent properties in the casting solution and provide better interaction between the macromolecular chains. Inorganic salts are also known to form complexes with the carbonyl group in polar aprotic solvents via ion–dipole interaction. Although there was research done previously on membranes made from doping Lithium chloride there hasn't been any membranes tested with calcium nitrate.

LiCl:

Lithium chloride (LiCl) is a salt and a typical ionic compound. The small size of the Li^+ ion gives rise to properties not seen for other alkali metal chlorides, such as extraordinary solubility in polar solvents (83g/100 mL of water at 20 °C) and its hygroscopic properties.

LiCl is expected to increase the membranes hydrophilicity due to its hygroscopic behavior, in previous studies it also showed increase in porosity, thinning of the porous layer and most importantly drastic positive changes in the rejection rates.

Previously LiCl was used to dope cellulose acetate (CA), polyamide, poly(vinylidene fluoride) (PVDF) and poly(ether sulfone) (PES) membranes. Hence it is important to study the effect of inorganic solvents like LiCl on PVC/PVB membrane hydrophilicity, morphology, permeability, porosity and most importantly selectivity. [13]

$Ca(NO_3)_2$:

Calcium nitrate ($Ca(NO_3)_2$), is also called Norgessalpeter (Norwegian saltpeter). This colorless salt absorbs moisture from the air and is commonly found as a tetra hydrate. It is mainly used as a component in fertilizers.

There has never been any prior research on the effect of $Ca(NO_3)_2$ as an additive on UF membranes. The doping of PVC/PVB membranes with calcium nitrate is expected to increase the hydrophilicity of the membranes because of its ability to attract water molecules. Therefore it is important to check how calcium nitrate doping affects the factors that determine the performance of a UF membrane.

Experimental Design:

The technique of uniform experimental design is a kind of space filling design that can be used for computer and industrial experiments where the statistical model of the responses is unknown. This is completely based on a simple cause and effect scenario. Engineers and scientists are constantly faced with the problem of distinguishing between effects that are caused by particular factors and those that arise from random error or just the building of a model between the input and output variables of a given experiment.

In recent years the traditional design methods are evolving to be simpler and more effective to solve more complex industrial problems. Most experimental design like orthogonal and optimal designs assume that the model is known with some unknown parameters like main effects, interactions and regression coefficients and choose a design such that the estimation of these unknown parameters have the highest efficiency. But in these cases the experiments domain might be too large and the two level designs might prove to be insufficient.

For example, taking a certain regression model into account:

$$y = g(x1, \ldots xs) + \in$$

Where, y is the response, g is the process model and represents a polynomial (first or second order) and Ɛ is the random error. When the mathematical function g is nonlinear and complex, an approximate linear model can be used to replace the original model.

$$y = gi(x1, \ldots xs) + h(x1, \ldots xs) + \in$$

Here, gi's are complex known parameters and h is a function that represents the deviation from the original. In lot of real life cases the gi's are unknown due to lack of knowledge of the process. Hence using a space filling uniform design method makes it easier to produce a more robust design.

The uniform design method was first proposed by Fang and Wang in 1978. Examples of successful applications of the uniform design method on improving technologies of various fields such as the textile industry, synthetic works, fermentation industry, pharmaceuticals manufacture, and some others have been consistently reported. The main difference between uniform design and traditional methods is that it is not defined in terms of combinatorial structure rather the spread of the design points over the entire design region. One advantage of the uniform design method over traditional statistical methods is that it can explore the correlation between factors and responses using a minimal amount of experimental runs. The Taguchi-type parameter method was found to be one of the more efficient design methods and is used to conduct the design of this particular research. For example, if an L_{36} (2^3X3^{11}) orthogonal array is used for inner and outer arrays, the total number of runs required would be 36*36 = 1296, while using $U_{13}(13^8)$ and $U_{12}(12^{10})$ uniform design the total amount runs would come up to 12*13 = 156. And more importantly, for practical ease, most uniform designs have been constructed and tabulated for users. [14]

The performance characteristics and evaluation parameters of the ultrafiltration membranes in this experiment is correlated with many parameters, such as, the nature, amount and blend of the polymeric material and additive used and temperature of the coagulation bath. For optimization of the fabrication conditions of these ultrafiltration membranes with good separation ability and high flux efficiency, ideally, a huge number of UF-membranes need to be prepared under all possible casting conditions if the trial and error method was used. Through the use of applied statistical method like uniform design, the amount of experiments that need to be conducted can be substantially reduced. Uniform design tables suitable for use in experimental design with up to seven predictor variables with five or more treatment levels in each are available. Therefore, using this method to optimize UF membrane performance would be extremely efficient and helpful.

Membrane Preparation:

UF membranes are prepared using phase inversion through immersion precipitation. Phase inversion happens between two miscible liquids and is the occurrence whereby the phases of a liquid-liquid dispersion interchange such that the dispersed phase spontaneously changes to become the continuous phase and vice versa under conditions determined by the system properties, volume ratio and energy input. The phase inversion process for an oil and water mixture is illustrated below:

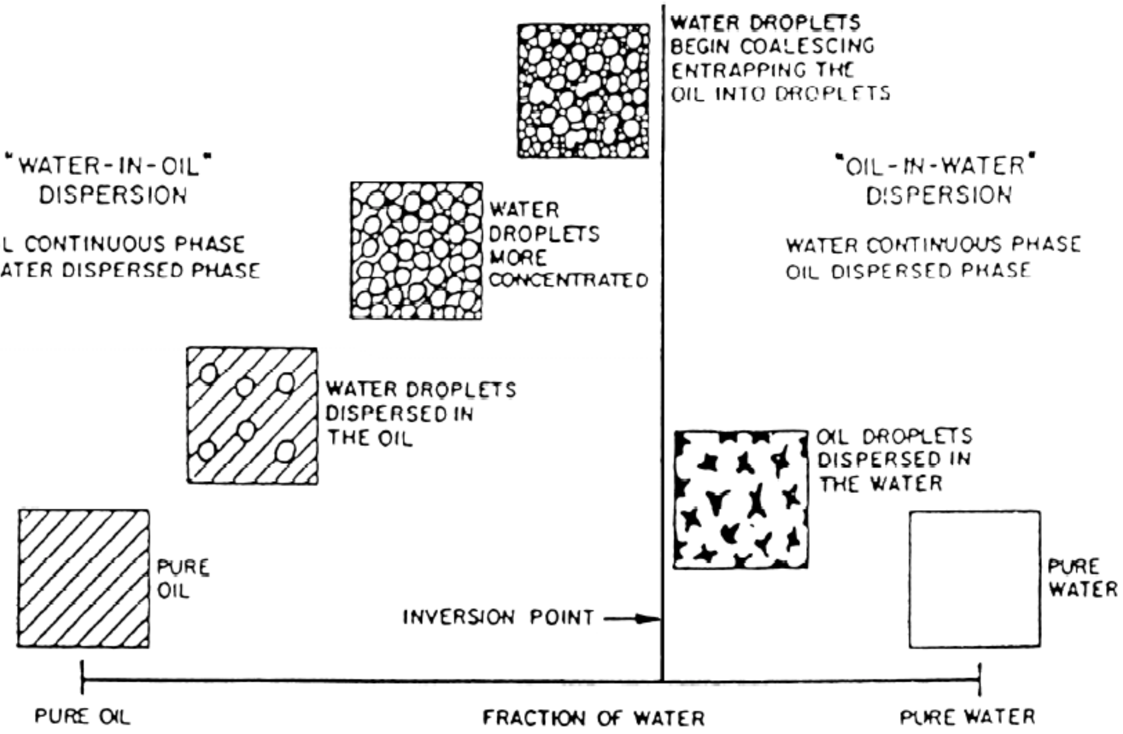


Figure 13: The phase inversion method illustrated using an oil-water example. (28: Matar)

The casting solution is referred to as the mixture of all the components (PVC/PVB/Additive) in the solvent being used (DMAc).The casting solution is generally molded into a certain form (flat sheet) and dipped into a coagulation bath after which phase inversion takes place. The phase inversion process follows the path illustrated below in the ternary phase diagram (Figure 12). The three extreme points represents the three components that come into play during a phase inversion process. That is polymer, solvent and the non-solvent which is water in this case. The initial casting solution (A) is a combination of the solvent and the polymers but during the phase inversion process the content of the solution changes. At point B the solvent precipitates out with the help of a few water molecules taking its place. At point C the membrane combination solidifies and finally reaches point D where all the solvent has phased out of the mixture and the membrane is a combination of the non-solvent and the polymer. This process is extremely spontaneous and takes place within a matter of 30 to 60s.[15]

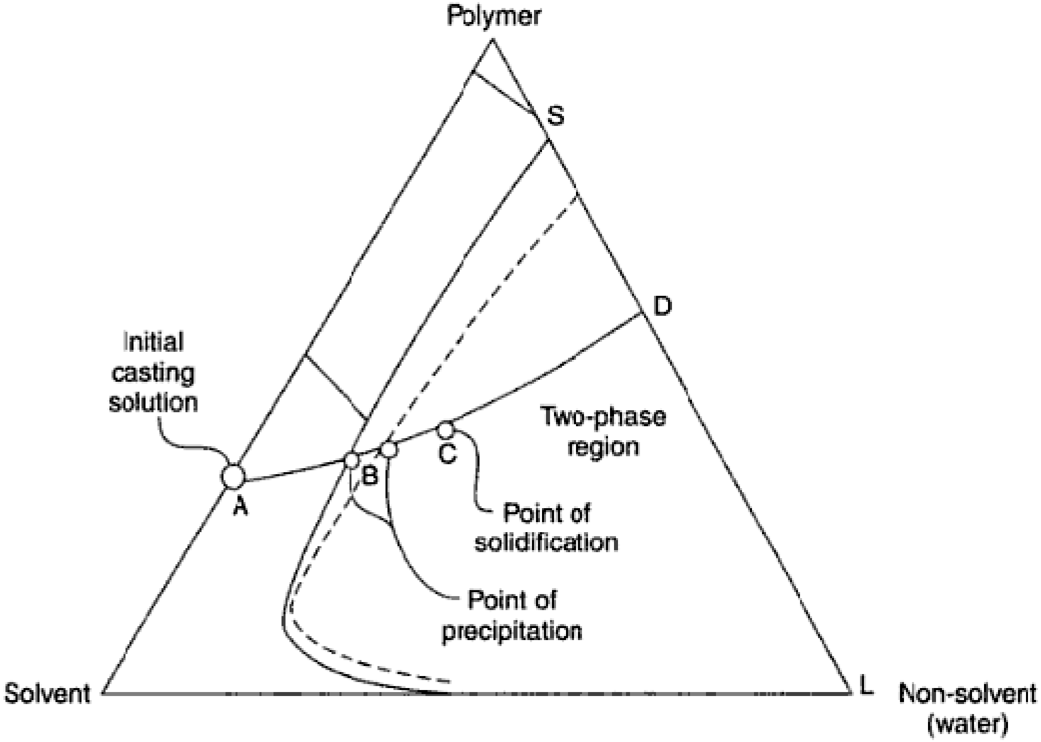


Figure 14: Ternary phase diagram representing the phase inversion process through immersion precipitation. (28: Matar)

Input Variables:

Experimental uniform design is first used to create an array of various combinations of the input variables being used in this research. For example:

Table 4: Example of a uniform design combination

Temperature of bath ®C (A)	PVC/PVB (Blend ratio) (B)	Weight % of Polymer (C)	Additive (D)	Weight % of Additive (E)
40	9:1	20	PVP	7

The input set points are defined below:

Weight percentage of the polymer:

The weight percentage of the polymer is the amount of the base polymer (PVC/PVB) that will exist in the casting solution and thereby the membrane itself. It can be found using:

$$Wt\%\ Polymer = \frac{PVC + PVB}{PVC + PVB + DMAc + Additive} * 100$$

PVC/PVB blend ratio:

The blend ratio or the relative amount of PVC and PVB is also used as a set point. This is calculated as a percentage of the total polymer being used. I. E.:

$$\%PVC = \frac{PVC}{PVC + PVB} * 100$$

$$\%PVB = \frac{PVB}{PVC + PVB} * 100$$

Additive:

This variable is simply a written input of the type of additive being used. (For reference on the types of additives being used please see Additives.

Weight percentage of the additive:

The weight percentage of the additive is the ratio of the additive against the mixture of all the components in the casting solution.

$$Wt\%\ Additive = \frac{Addtive}{PVC + PVB + DMAc + Additive} * 100$$

Water bath temperature:

After all the different components are mixed according to the different input variables defined above the casting solution is generally stirred in a water bath. The temperature of the water bath can influence crystallinity, viscosity and even the overall performance of the membrane. Hence, this was set as a variable and changed to see the effect that might have on the performance of the different membranes.

Characterization:

In an ultrafiltration membrane experiment the characteristics of a membrane can be done using many different output variables. For this experiment, effect and cause relationships were studied according to the output parameters defined and illustrated below:

Viscosity of the Casting Solution:

The viscosity of the casting solution is measured directly by using a viscometer. Viscosity helps determine the miscibility/compatibility of the components in the casting solution. If the correlation between the viscosity of the casting solution and the different blends of PVC and PVB is linear the components are completely miscible. For a non-linear relation the polymers are partly miscible and of course for a S-segment relation the polymers are fully immiscible. Also In the case of this research the miscibility of the polymeric additives can be determined by variations in these correlations.

The viscosity variations among different casting solutions can help predict the tensile strength of the membrane. A relatively higher viscosity would mean the production of a stronger membrane, while a lower viscosity means a weaker membrane might be produced.[2]

Porosity of the membrane:

Porosity is the measure of void spaces in a certain material. It is simply the fraction of the volume of voids over the total volume of the material (including the voids). Porosity can be calculated using the following equations:

$$Porosity = \frac{Volume\ of\ void}{Volume\ of\ void + volume\ of\ material}$$

In real life using mass difference of the wet and dry material is used to make the porosity calculations

$$\boldsymbol{Porosity} = \frac{(\boldsymbol{W2}) - (\boldsymbol{W1})}{\boldsymbol{\rho met * Vm}} \quad \text{Equation 1}$$

Where, W2 = weight of the wet membrane

W1 = weight of the dry membrane

$$\rho met = Density\ of\ the\ combined\ membrane\ material$$

$$Vm = Volume\ of\ the\ membrane$$

Flux of pure water through the membrane:

The flux through the membrane is the measure of how fast the membrane can process the water that is being passed through it. Flux is measured in volume of water per unit area per unit time. This is one of the most important characteristics of a membrane since in an industrial sized application a huge amount of fluids need to be processed so, the larger the flux of a membrane the more advantageous it is.

Usually flux is measured using a dead end stirred cell ultrafiltration system. The water is held in a filtration cell and the pressure gradient is created by pumping gas at a certain pressure into the cell. The water is accumulated on a beaker sitting atop an electronic balance. The amount of time required for all the water to move into the beaker and the mass change on the balance are the two values that are recorded.

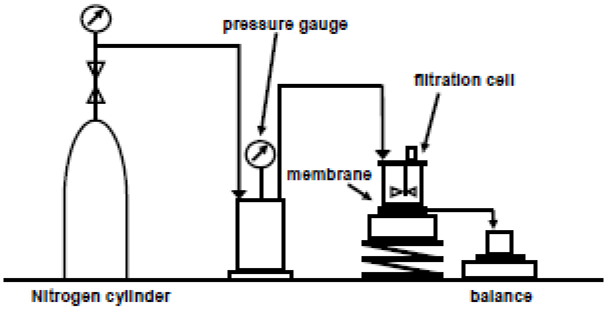


Figure 15: Dead end stirred cell ultrafiltration system to measure flux. (29: Becht)

The flux through the membrane can be calculated using this formula:

$$Flux, Jw = \frac{V}{A*t} \quad \text{Equation 2}$$

Where, V = volume of the water filtered

A = the area of the membrane

t = time required for complete filtration

Rejection of particles by the membrane:

The main function of a membrane is its selectivity against large sized particles. This is the most important characteristic of a membrane. The amount of particles that a membrane can block means the purer the fluid is on the permeate side.

Rejection can be calculated using:

$$\boldsymbol{Rejection} = \left(\mathbf{1} - \left(\frac{Cp}{Cf}\right)\right) * \mathbf{100} \quad \text{Equation 3}$$

$$here, Cp = Concentration\ of\ the\ permeate$$

$$here, Cf = Concentration\ of\ raw\ water$$

Scanning electron microscopy:

A scanning electron microscope (SEM) is a type of electron microscope that images a sample by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms of the material being tested producing signals that contain information about the sample's surface topography and composition.

SEM images are used in the case of ultrafiltration membranes to check the morphological changes that a certain membrane undergoes due to the different component combinations. A scanning electron microscope is particularly helpful in the case of UF membranes because it helps identify the anisotropic and asymmetric nature: the voids and the void walls are clearly visible in the supporting substructure of the membrane.[16]

Fourier transformed infrared spectroscopy:

Fourier transform infrared spectroscopy (FTIR) is a technique which is used to obtain an infrared spectrum of absorption, emission, photoconductivity or Raman scattering of a solid, liquid or gas. An FTIR spectrometer instantaneously collects spectral data in a varied spectral range. This deliberates a significant advantage over a dispersive spectrometer which measures intensity over a narrow range of wavelengths at a time.

FTIR is extensively used in UF membrane studies to check the functional groups of components in the bulk of the membrane. This can help identify forces that attract foulants and also predict the tensile strength of the components.[17]

Contact Angle:

The contact angle is the angle at which a liquid/vapor interface meets a certain solid surface. In the case of UF membranes it is the measure of hydrophilicity/hydrophobicity of the particular membrane.

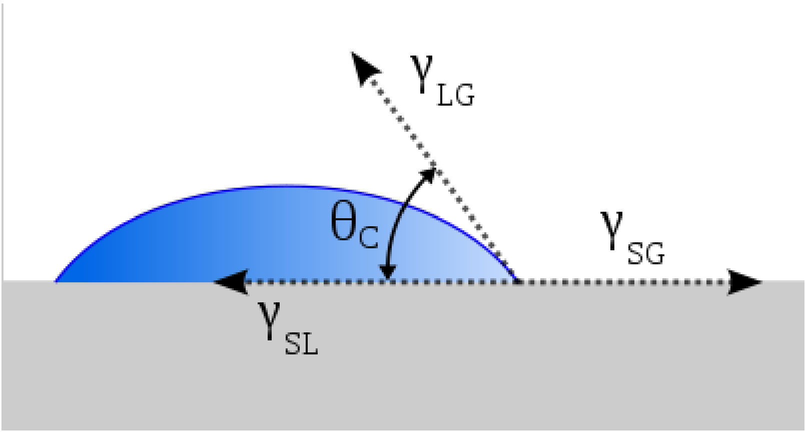


Figure 16: The contact angle of the membrane
(30: Absoluteastronomy.com)

Here, ϒsl = solid-liquid interface energy

ϒlg = liquid gas interface energy

ϒsg = solid-gas interface energy

Ɵc = contact angle

For reference: For any given membrane an angle above 90 degrees means lower likeness towards water and more hydrophobic but anything less than that means the membrane is more hydrophilic.

Atomic force microscopy:

Atomic force microscopy or AFM is a very high resolution type scanning probe microscopy. In a AFM there is a certain tip attached to the end of a cantilever. This tip probes the surface of the underlying material. The cantilever acts like a spring and the force differentials which it undergoes is used to create a topographical image of the surface of the material.

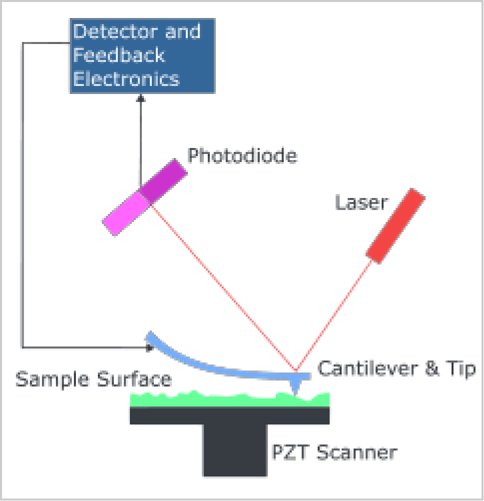


Figure 17: AFM mechanism
(31: iap.tuwien.ac.at)

There are many advantages of using AFM imagery in the case of UF membranes.

1) A three dimensional image of the membrane surface can be attained
2) The images produced is of a higher resolution than other microscopic imaging techniques

This can help us study many factors that affect the make of a certain membrane. Quantities such as pore distribution, pore size, surface roughness and so forth.

Methodology

Uniform design and component combination tables:

The initial step for performing an optimization study on UF membranes was the designing of the experimental combinations to make the different casting solutions. As mentioned before the Taguchi's parameter type uniform design is used and for this technique the parametric combinations are pre tabulated.

The first step was using Table 2 ,Appendix A which identifies according to the number of factors the column numbers in the U_{11} (11^{10}) table (Table 3,Appendix A) that need to be used. (Deng Bo 1994). The final numerical statistical combination would look like that given in Table 4, Appendix A.

As it can be seen the factors were named according to letters going from A to E and each factor has 5 levels. This means that every factor has five different values. These factor levels are defined in Table 5, Appendix A. The complete correlation of the factors and levels are shown according to the matrix in Table 6, Appendix A. So for example, from this table the numerical value of 1 and 2 in the statistical combination table will relate to the same level of a certain factor. These factor and level definitions are used in correspondence to the numerical values of Table 4, Appendix A. And the final combination is represented in Table 7, Appendix A. The values represented under A1, B2 and so forth are substituted in to produce the final set of design combination that is used to make the different casting solutions (Table 2, methodology).

Table 5: The final set of design combination used to create the different casting solutions.

Experiment	Temperature of bath (A)	PVC/PVB (Blend Ratio)(B)	Wt.% of Polymer(C)	Additive (D)	Wt. % of Additive. (E)
1	40	9:1	20	PVP	7
2	40	8:2	18	LiCl	3
3	50	7:3	10	PEG 1000	10
4	50	6:4	21	LiCl	5
5	60	5:5	20	PEG 1000	1
6	60	9:1	15	CaNO3	10
7	70	8:2	10	PEG 600	5
8	70	7:3	21	CaNO3	1
9	80	6:4	18	PEG 600	7
10	80	5:5	15	PVP	3

Membrane Preparation:

The different steps that were used to prepare a certain membrane are defined below.

Measurement of DMAc, PVC, PVB and additive amounts:

Since most of the factors are represented in percentage or ratios, the exact amount to put into a mixture needs to be calculated. Microsoft Excel, one of the most commonly used spreadsheet software was used to make this process more efficient.

The main problem in finding the amounts of additive and polymer is clear when one looks at the equation to find the weight percentage of either additive or the polymer.

$$Wt\%\ Polymer = \frac{PVC + PVB}{PVC + PVB + DMAc + Additive} * 100$$

$$Wt\%\ Additive = \frac{Addtive}{PVC + PVB + DMAc + Additive} * 100$$

In order to determine the amount of polymer or additive one has to know the total weight when everything is combined but that cannot be determined without finding the amount of polymer or additive itself. In order to do this a system of simultaneous equations was created which was solved for each and every experimental run according to the defined weight percentages and amount of DMAc. The sample calculation is shown in appendix B.

Finally after the amount of polymer was figured out the amount of the individual PVC and PVB amounts are calculated according to the equation:

$$Amont\ of\ PVC = (PVC + PVB) * \%PVC$$

$$Amount\ of PVB = (PVB + PVC) * \%PVB$$

Membrane Preparation:

As mentioned before the PVC/PVB/Additive composite UF membrane was mixed using a phase inversion method. All the membranes were prepared according to the following steps:

1) The DMAc was poured into an Erlenmeyer flask sitting atop a mass balance used to measure the amount of DMAc.
2) The powdered form of each of the components i.e. PVC, PVB and additive was weighed on a mass balance according to the required amount calculated using the spreadsheet software.
3) The PVC and PVB was gradually poured into the flask containing the DMAc and simultaneously stirred to attain proper mixing.
4) The polymeric additives were mixed with the solvent in the same way but for the inorganic solvents initial vacuum drying was required to remove the water content.
5) After all the components are mixed in the flask, the viscous liquid was continuously stirred in a water bath at a certain temperature. (This water bath temperature is one of the factors being varied in the experiment)
6) Each casting solution was continuously stirred in the water bath for 12 -36 hours until it was completely mixed.
7) After proper mixing the casting solution was poured onto a glass pane sitting atop a membrane scraper. The viscous gel is scraped to form a layer over the flat glass pane.
8) This glass pane with the gel layer was immediately dipped into the coagulation bath and the instantaneous formation of the membrane is observed.
9) The membrane was stored in the coagulation bath for a longer period of time for complete removal of all the solvent. These membranes were cut into smaller pieces according to the characterization requirement.
10) The same steps were followed to produce each UF membrane 4 different times for result verification.

Characterization method:

Viscosity of the Casting Solution:

The viscosity of the casting solution was directly measured under a viscometer. The viscosity is measured according to the following steps:

- The viscometer used a certain spindle that went into the casting solution and the spindle size is decided by an educated guess of how viscous the material might be. The spindle sizes go from 30 to 35 and the smaller number represents a larger spindle used for less viscous gels.
- The appropriate spindle was put the solution and the viscometer was run at a certain percentage of the original RPM.
- The speed was adjusted until the viscometer gave a stable reading.
- Reading was taken for 5 different RPM's for each solution and the average viscosity was taken into consideration for further study.

Porosity of the membrane:

The porosity was calculated according to the equation 1. The procedure to attain the values to calculate porosity is given below:

- The membranes were cut into equal pieces and the dimensions were measured using a measuring tape and the thickness was measured using a sensitive slide caliper.
- Then the membranes were dipped into water until they were completely soaked.
- The weights of the individual membrane pieces were measured and they were placed on a glass pallet.
- The glass pallet was placed inside an oven and heated up 45 degrees C. The membranes are dried for a while
- Then the weight of the membrane was measured in intervals of heating until the weight did not fluctuate any more.
- Using the difference in the initial and final weights, the volume and density of the material the porosity of the membrane was measured.

Flux of pure water through the membrane:

The pure water flux through the membrane is calculated using equation 2. As mentioned before the variables in the equation were measured using a dead end stirred cell filtration system. The filtration runs were conducted according to the following steps:

- The membrane was placed inside the dead end stirred cell and the cell was filled with distilled water.
- The pressure was applied on the water in the cell by pumping gas from a gas cylinder into the cell.
- After the pre-pressure value of 0.12 MPa was reached the pressure is lowered to work at 0.1 MPa.
- The effluent water was collected in a beaker sitting atop an electronic mass balance connected to a computerized system.
- This automatic data logging software measures the time and the change in weight the balance undergoes through this time period.

Rejection of particles by the membrane:

The rejection of the membrane was calculated using equation 3. The variables of the equation were found following these procedures:

- The concentration of the protein solution was figured out using a UV-spectrophotometer. This machine gives the amount of absorbance according to a certain concentration of a solution. Hence a reference absorbance calibration chart was needed to correlate absorbance with protein concentration.
- The absorbance chart was prepared by dissolving 0.1 gram of BSA protein in 10 ml of water creating a 10mg/ml solution of BSA (Bovine serum albumin).
- Different amounts of this solution were used with different amounts of a PBS buffer solution to create different concentrations of protein solution. The sample calculation to reach a certain concentration is given in Appendix B and the calibration graph is presented in Appendix C.
- A protein solution of concentration 1000 mg/l was used for rejection calculation.
- The protein solution was used in the same dead end stirred cell filtration system used to measure flux.
- The initial and final absorbance values were measured and used in the calibration graph to find the values of Cp and Cf.

Scanning electron microscopy:

For the SEM process the membranes were cut into small pieces and adhered to a miniature ring shaped solid object. It was placed into a boxed slot which was pushed into the SEM and the chamber was vacuum pumped. The images were automatically rendered onto imaging software.

Fourier transformed infrared spectroscopy:

Individual membrane pieces were placed under a certain probe which was pushed onto the surface of the membrane. The readings were automatically taken by the machine and the absorbance bands were graphically represented.

Contact Angle:

The contact angle of each membrane was found using a CA goniometer. Membranes were dried and cut into square pieces and placed under a needle. 20ul of water was dropped onto the membrane and the blown up image of the water droplet on the membrane was taken.

Atomic force microscopy:

The AFM images were taken automatically by a computer. The membranes were placed directly under the tip attached to the cantilever. The computer processes the readings taken by the AFM tip and a rendered 3 dimensional image is produced.

Results and discussions:

In this section the results of the different characterization techniques and their significance to the design of the membrane will be discussed

SEM:

SEM imagery was used as a visual verification of how the combinations of polymer and additives influence the morphology of the membrane. The SEM images of membranes # 1- 10 are consecutively illustrated below.

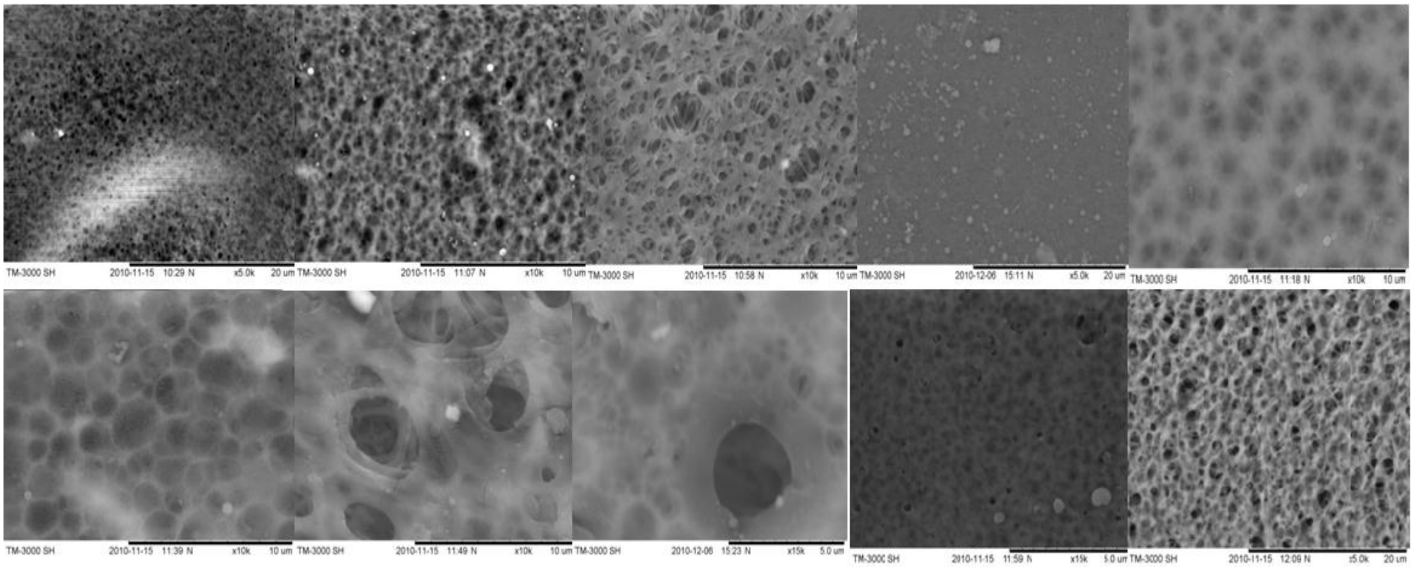


Figure 18: SEM: 1(TOP LEFT) - 10 (BOTTOM RIGHT)

CA:

The contact angle for the membranes was used to check the hydrophobicity/hydrophobicity. This is compared to the relative amount of components which influence the value.

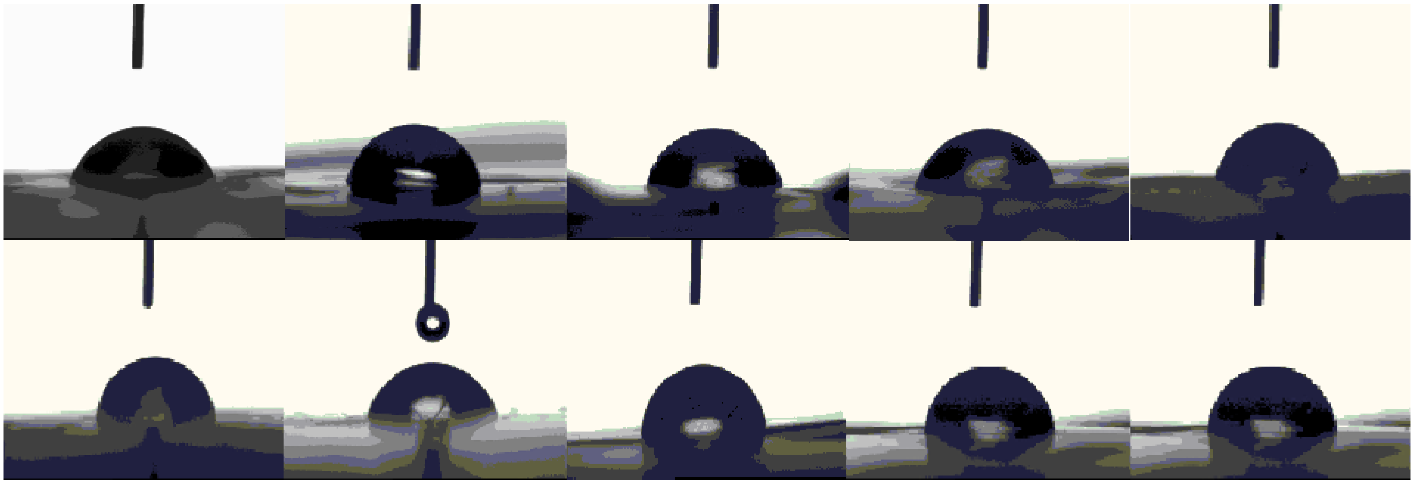


Figure 19: CA: 1(TOP LEFT) - 10(BOTTOM RIGHT)

Table 6: Exact amounts of components added to make up the membrane

Experiment	Additive (D)	Amount PVC(g)	Amount PVB(g)	Amount additive (g)	CA degrees
1.0	PVP	61.8	15.5	27.1	72.0
2.0	LiCl	32.7	8.2	6.8	78.0
3.0	PEG 1000	24.8	10.6	35.4	75.0
4.0	LiCl	31.6	21.1	12.5	70.0
5.0	PEG 1000	35.8	35.8	3.6	81.0
6.0	CaNO3	49.2	5.5	36.4	91.0
7.0	PEG 600	26.7	6.7	16.7	72.0
8.0	CaNO3	53.2	22.8	3.6	82.0
9.0	PEG 600	40.8	27.2	26.4	83.0
10.0	PVP	26.0	26.0	10.4	69.0

These surface SEM images only display the top porous surface image. As it can be seen the pore distribution and morphology is very clearly illustrated on the membrane images. And the CA images shows how much the micro bubble of water is sticking out of the membrane which is the measure of hydrophilicity. In addition, for reference the amount of each component and the corresponding CA are tabulated above in Table 3.

Membrane 1: This membrane is extremely porous and the pores on the membrane are fairly evenly distributed .This means that there might be a good balance between retention, flux and tensile strength. The amount of PVC used for this membrane is fairly high and can be used to explain the high stress that it can with stand. The amount of PVB is lower than it counterpart membrane # 10 which explains the relative lack of hydrophilicity. Then again, the relation between CA and the amount of PVB is fairly evident since the more PVB that is used the more hydrophilic the membrane acts.

Membrane 2: This is one of the membranes produced from an inorganic additive. The complexes formed by the Li ion shows as the small white spots on the surface. The complexes are fairly low because of the lower amount of additive than its counterpart, membrane # 4. This is another membrane with numerous pores but they are also very evenly distributed. This verifies the good balance between tensile strength and flux of the membrane. The CA shows that because of the decrease in PVB this membrane is less hydrophilic.

Membrane 3: The pores are extremely large and the SEM image is able to show the entanglements within inner layers through the surface. The pores are not very even and it is evident that the low tensile strength will make this membrane prone to breakage giving it a high flux but extremely low retention. The amount of PVC and PVB used to make this membrane is very low. But the CA follows the trend of proportionality with the amount of PVB.

Membrane 4: This is another membrane made from the LiCl additive and the complexes on the surface are much clearer. This membrane is much less porous and hence is predicted to have a large selectivity but extremely low flux. The membrane is extremely hydrophilic because of its low CA, this is because of the increased amounts of complexes due larger amount of LiCl and PVB compared to membrane 1,2 and 3.

Membrane 5: This membrane consists of equal amounts of PVC and PVB. The casting solution proved to be extremely viscous and the membrane dried up rapidly when open to the atmosphere. The amount of pores are extremely limited but are evenly distributed over the surface of the membrane. This membrane is more hydrophobic, given the high CA. This might be because of the high amounts of PVC and/or PEG is often acts as a macro void suppressor rather than a hydrophilic agent.

Membrane 6: This was one of the hardest membranes to run tests on. It is very evident that the membrane is extremely weak because of the dilated pores illustrated on the surface image. The contact angle also shows that this membrane is hydrophobic. This may be because of the excessive amounts of PVC and also the CaNO3 additive did not prove to be an appropriate novel material.

Membrane 7: For this membrane PEG 600 worked as a good hydrophilic agent. The hydrophilic characteristic properties can be explained by the low amounts of PVC but the relative high amounts of PEG. The magnified surface image shows that although the pores are dilated the strength of entanglement should be high enough to hold the membrane together for a high flux.

Membrane 8: This is the second membrane made from CaNO3. Although the amount of the calcium nitrate is much less, the amount of the PVC is fairly high. From this we can conclude that CaNO3 in high amounts will work towards hydrophobic characteristics of the membrane. The surface image also shows the dilated pores that were prone to breakage when it underwent high pressures.

Membrane 9: The fairly high amounts of PVC make this membrane fairly hydrophobic. The surface image shows that it’s not very porous which verifies that this membrane will have high amounts of retention but a very low flux.

Membrane 10: This membrane is the most hydrophilic one of the group. The fairly high amounts PVB, low PVC and PVP might be the cause of this character. The membrane surface is extremely porous with these pores being evenly distributed. This can help with a good balance between flux and rejection. This membrane is expected to have less swelled voids than membrane # 1 because of the lower amounts of PVP.

FTIR:

To check the polymeric functional groups which exist within the membrane a Fourier transformed Infrared spectroscopy was conducted on each membrane. This can help explain the exact compounds which affect the forces of attraction with the retained particles and which holds the polymers together.

The FTIR responses and the different functional groups represented by the different peaks are illustrated below:

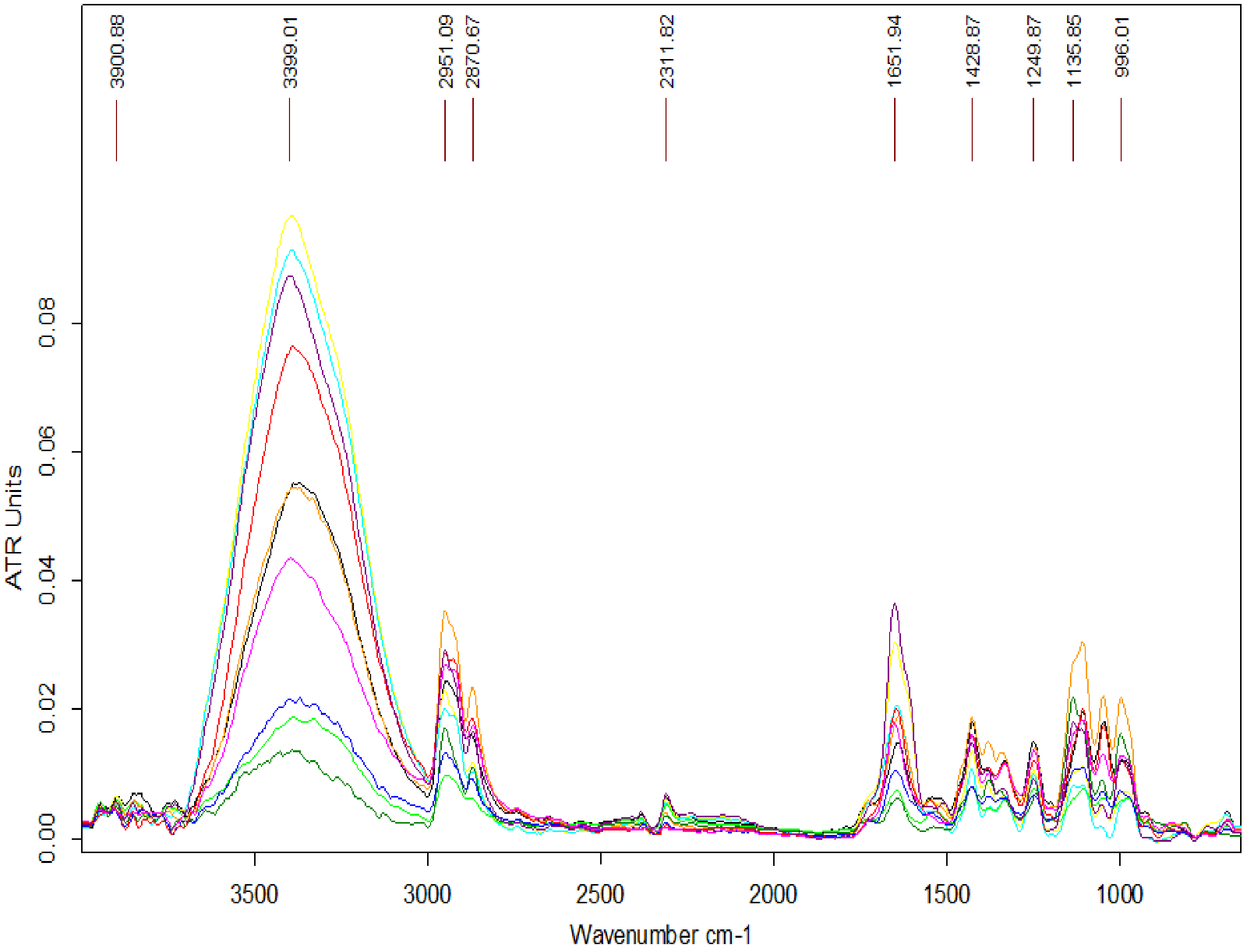


Figure 20: FTIR spectroscopy

All the membranes have very similar IR band peaks mainly because of the similar composition of PVC and PVB but there are some unusual changes to the intensity of the peaks or ATR units because of interaction with the additives or the amount of materials used. The membrane labels and the peak positions with their corresponding functional groups are tabulated below.

Table 7 : Peak position according to Fig 18 and Functional groups

Peak position wavenumber cm^{-1}	Functional group possibilities
3399.01	Alcohol or phenol broad stretch (3550 – 3200)
2951.09	Carboxylic Acid -O-H broad stretch (3000 – 2500) Alkyl C-H medium Stretch (2950 – 2850)
2311.82	Phosphine –P-H stretch (2320-2270)
1651.94	Amides –C=O stretch, -N-H bend (1680-1550)
1428.87	Esters –C=O stretch (1440-1400)
1249.87	Acetates C-C(O)-C stretch (1260-1230)
1135.85	Alcohols –C-O stretch (1260-1000) Ethers C-O-C stretch (~1120)
~750	Alkyl halides, acid chlorides –C-Cl (785-540)

After specifying the functional groups represented by each peak positions it is important to distinguish the membranes and discuss the peaks, stretch intensity and the peak intensity to show how the additives reacts with PVC and PVB to give the membrane its individual characteristics.

Table 8: Color coded FTIR spectroscopy and compounds present.

Membrane # (color coded)	Compounds present
1 (Pink)	$(-CH_2-CHCl-) + (-CH_2-R_1-)(-CH_2-CHOH-)(-CH_2-CHO-CO-CH_3)+(-CHNR_2O-CH_2-)$
2 (Red)	$(-CH_2-CHCl-) + (-CH_2-R_1-)(-CH_2-CHOH-)(-CH_2-CHO-CO-CH_3)+LiCl$
3 (Blue)	$(-CH_2-CHCl-) + (-CH_2-R_1-)(-CH_2-CHOH-)(-CH_2-CHO-CO-CH_3)+H-(O-CH_2-CH_2-)-O-H$
4 (green)	$(-CH_2-CHCl-) + (-CH_2-R_1-)(-CH_2-CHOH-)(-CH_2-CHO-CO-CH_3)+ LiCl$
5 (orange)	$(-CH_2-CHCl-) + (-CH_2-R_1-)(-CH_2-CHOH-)(-CH_2-CHO-CO-CH_3)+ H-(O-CH_2-CH_2-)-O-H$
6 (L. green)	$(-CH_2-CHCl-) + (-CH_2-R_1-)(-CH_2-CHOH-)(-CH_2-CHO-CO-CH_3)+ CaNO_3$
7 (L. blue)	$(-CH_2-CHCl-) + (-CH_2-R_1-)(-CH_2-CHOH-)(-CH_2-CHO-CO-CH_3)+ H-(O-CH_2-CH_2-)-O-H$
8 (Yellow)	$(-CH_2-CHCl-) + (-CH_2-R_1-)(-CH_2-CHOH-)(-CH_2-CHO-CO-CH_3)+ CaNO_3$
9 (Black)	$(-CH_2-CHCl-) + (-CH_2-R_1-)(-CH_2-CHOH-)(-CH_2-CHO-CO-CH_3)+ H-(O-CH_2-CH_2-)-O-H$
10 (Purple)	$(-CH_2-CHCl-) + (-CH_2-R_1-)(-CH_2-CHOH-)(-CH_2-CHO-CO-CH_3)+(-CHNR_2O-CH_2-)$

Membrane 1 and 10: The peaks at the 3350-3400 cm^{-1} and ~740 cm^{-1} can be explained by the constant presence of –OH from PVB and the –CL from PVC. The amount of PVB is much more in membrane 10 is more than in membrane one and hence the phenol peak for 10 is much higher.

The peak at around ~1650 cm^{-1} is produced by the functional group of –N-C=O- and by a simple –C-C- bond. Although the amount of PVP present in membrane 1 is much higher the peak intensity is much less. This can be explained by the excessive amounts of PVC for which there would much more –C-C- bonds present. Hence for a membrane made with PVC/PVB/PVP it can be predicted that a higher peak intensity at the nitrile and phenol positions can result in lower contact angles and higher hydrophilicity.

Membrane 2 and 4: The amount of PVB increases from membrane 2 to 4 which means there is an excessive amounts of –OH in 4 but the peak intensity at ~3350 cm^{-1} for 4 is much less. This can be explained by the complexes formed by the presence of LiCl. In small amounts the LiCl makes the phenols more accessible while in excess amounts the phenols are suppressed under the complexes and hence results in the smaller peak intensity which is also supported by the contact angle. One of the more significant peaks for membrane 4 is at ~1135 which occur because of the alcohols (-C-O-) and ethers (-C-O-C-) present in the mixture. The excessive amounts of PVC/PVB relative to membrane 2 explains the excessive amounts of –C-O and –C-O-C- bonds present in membrane 4 and the higher peak intensity at ~1130.

Membrane 3 and 5: These membranes were formed from PEG-1000. For all the peak positions the peak intensity is much lower for membrane 3 than membrane 5. This can be explained by the increase in amounts of PVB which gives the excessive amounts of –OH and the increase in the amount of PVB /PVC which counts for the increase in –C-O and –C-O-C- bonds. This also proves that the excessive amount of PEG for membrane 3 does not help with the peak intensities but does make the membrane more hydrophilic.

Membrane 6 and 8: Membrane 8 has one of the highest amount of PVB which gives a significantly high amounts of phenols and hence the high peak intensity. In small amounts the $CaNO_3$ complexes help make the phenols more accessible and the membrane more hydrophilic. With the combination of excessive PVC , low amounts of PVB and high amounts of calcium complexes makes membrane 6 extremely inappropriate for use and hydrophobic.

Membrane 7 and 9: Although the amount of PVB in membrane 9 is more, the increased amounts of additive in membrane 7 accounts for its high peak intensity at ~3390 cm^{-1}. Membrane 9 has a relatively higher peak at ~2950 which accounts for the increased amounts of carboxylic acid functional group present in the membrane. The membrane peak intensity accounts for the contact angle difference and membrane 7's increased hydrophilicity.

AFM:

The atomic force microscopy was performed on the membranes with the best performance, namely membranes 2, 7, 8, 9 and 10. The surface roughness and pore depths are illustrated through the 3-Dimensional images shown below.

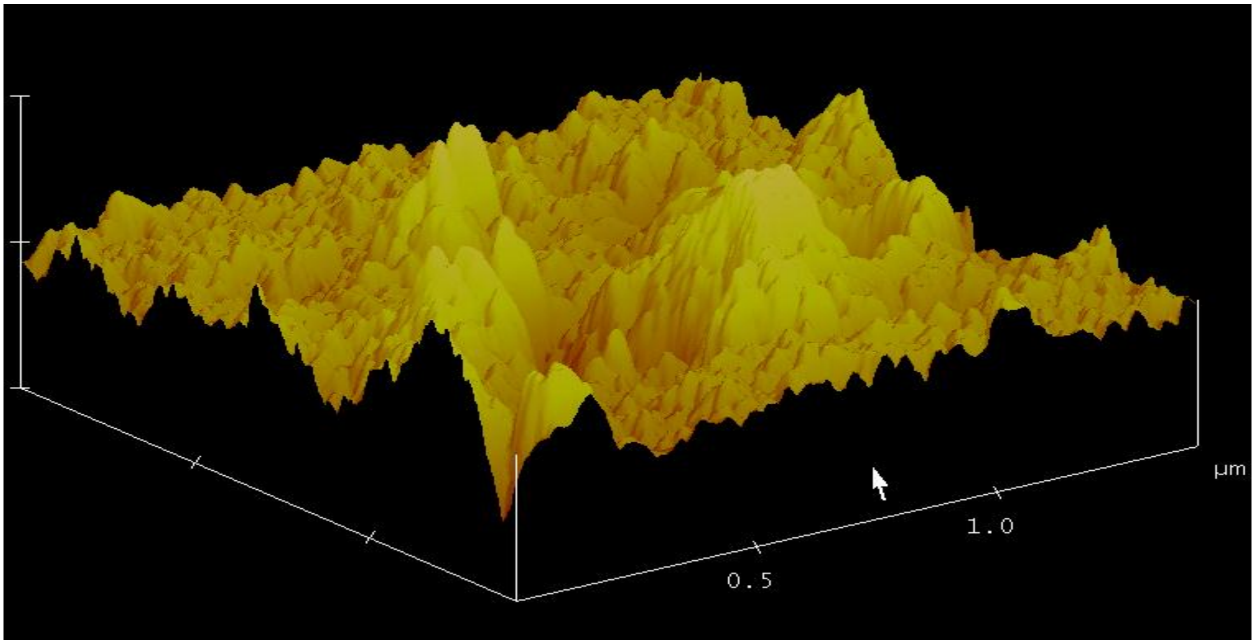


Figure 21: Membrane2

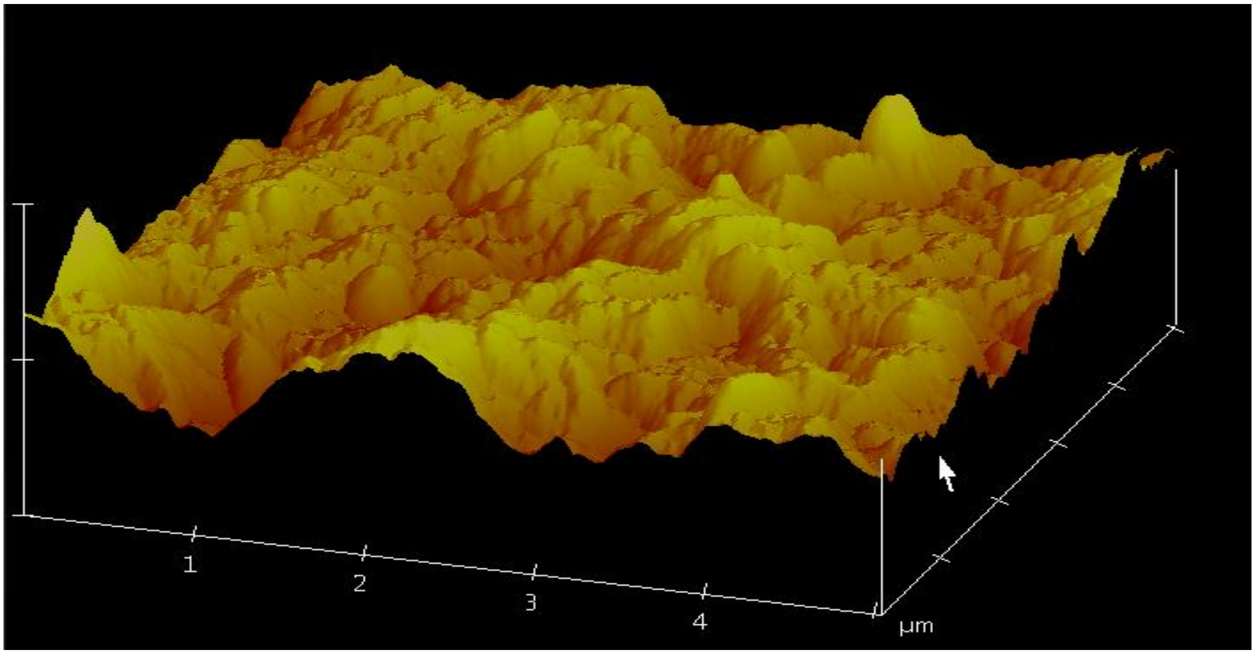


Figure 22: Membrane 7

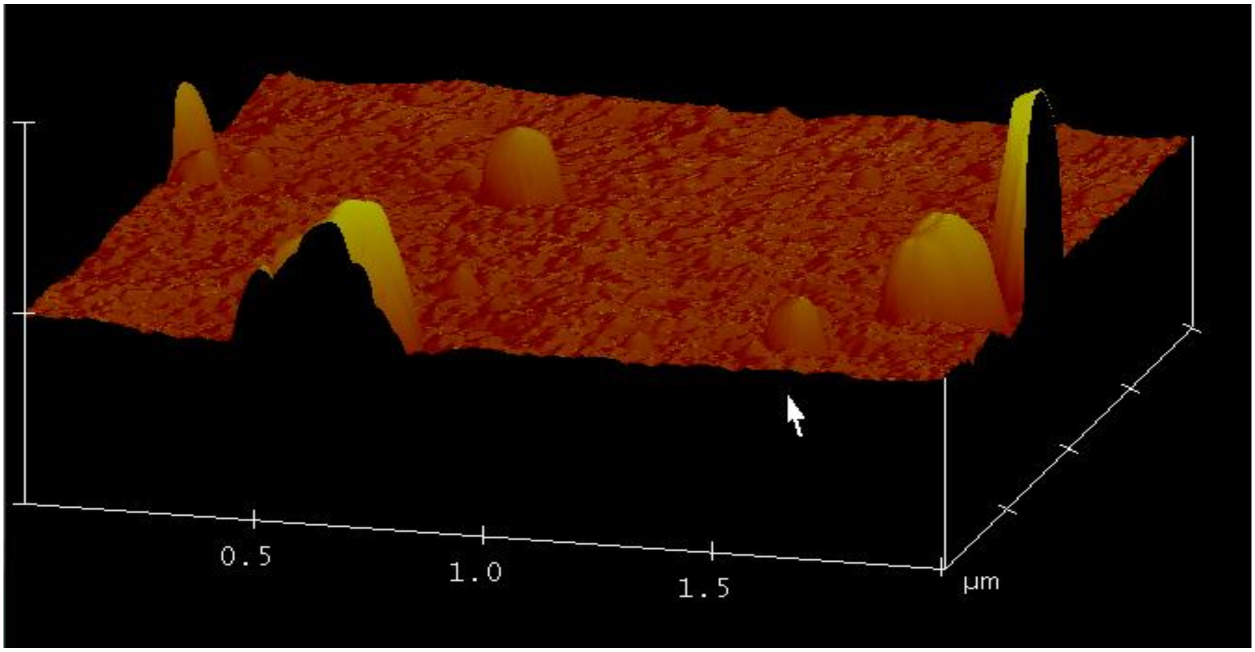


Figure 23: Membrane 8

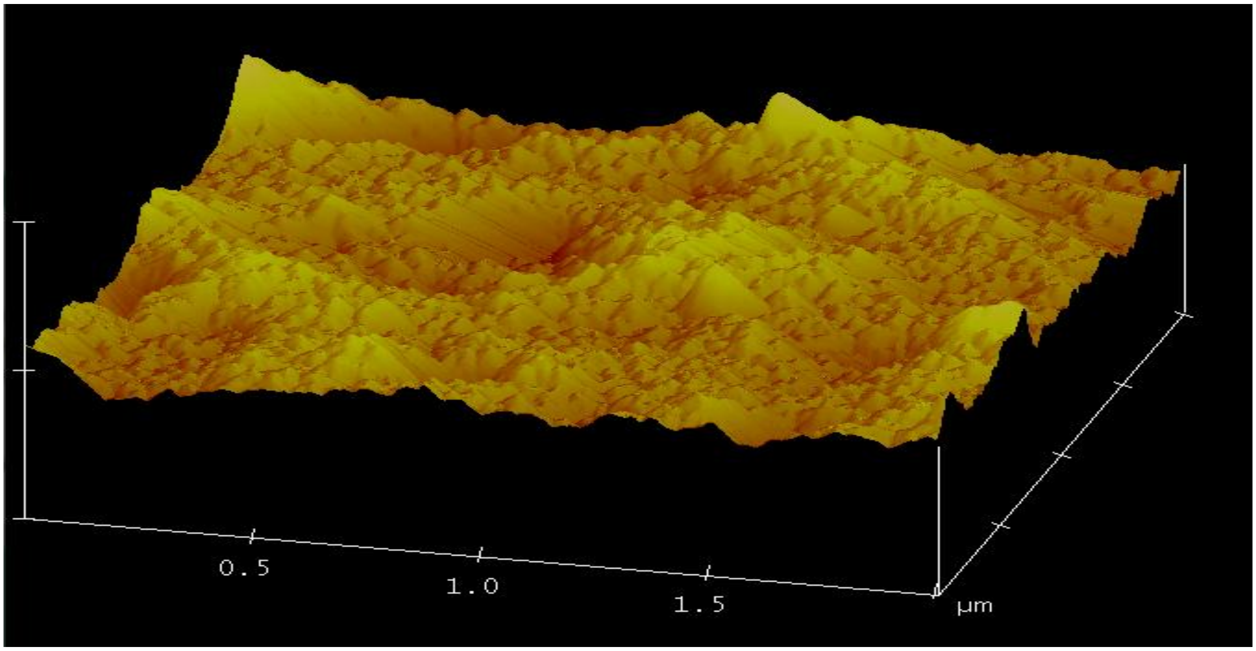


Figure 24: Membrane 9

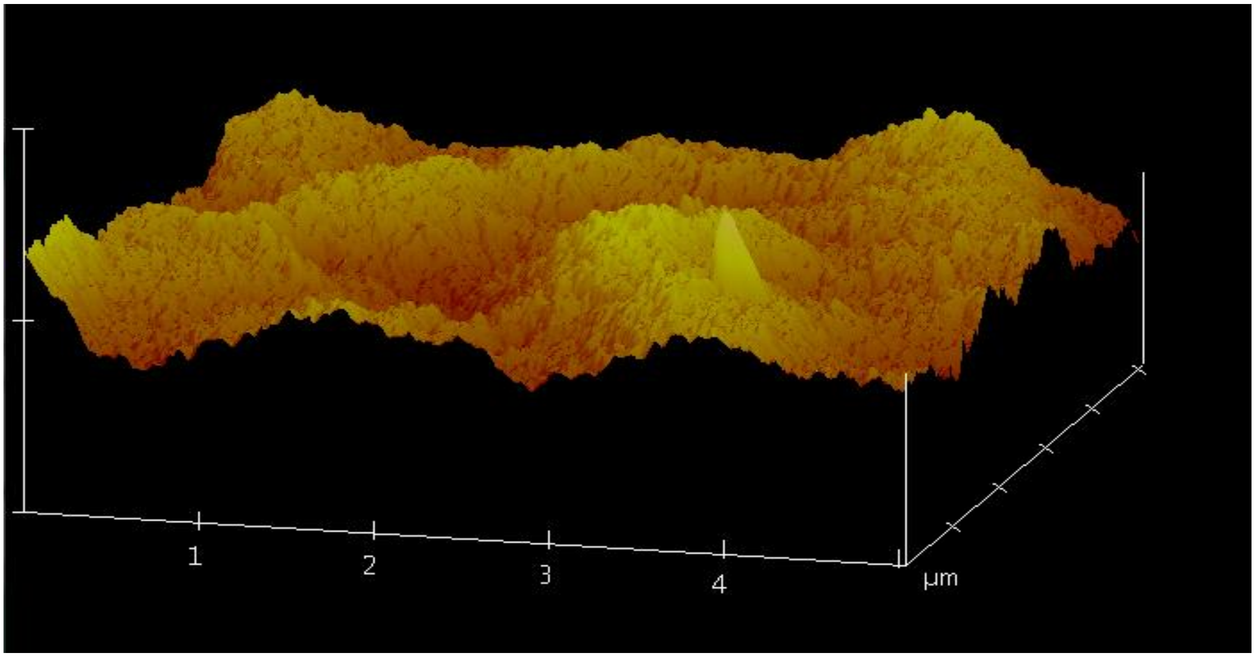


Figure 25: Membrane 10

It is important to consider how the surface roughness and the pore depth affect the membranes flux and rejection.

Table 9 : Membrane pore depth

Membrane #	Average Pore depth (nm)	Average peak to peak distance (nm)	CA	Flux	Rejection
2	41.88	1.942	78	89.1	52.12
7	289.43	25.017	72	534.672	30.45
8	477.76	3.525	82	142.38	72.57
9	55.454	0.667	83	214.776	70.35
10	88.255	4.209	69	889.272	34.31

As it can be seen the more the CA the more the flux and it is generally known that rejection is inversely proportional to flux. The flux and rejection depends directly on the pore depth and on the intermolecular forces between the particles and the membrane materials.

Membrane 2 : It is safe to predict that the complexes formed by LiCl on membrane 2 are repelling the water particles making it more hydrophobic and giving it a low flux capacity but this helps increase the concentration of the permeate.

Membrane 7: The average pore depth of membrane 7 is relatively large which was predicted before from the SEM images. But the pores are spread out more than all the other membranes. So although flux is large the amount of proteins being rejected is fairly low.

Membrane 8: With a large pore depth and very closely located pores this membrane has a slightly low flux because of the excessive amounts of PVC used to produce it which also gives it the low hydrophilic characteristics. Never the less, membrane 8 has a high rejection rate which proves it to be more useful in the industry.

Membrane 9: The pores are smaller in membrane 9 but are extremely close to each other which gives it a relatively higher flux which in turn also hampered by the low hydrophilicity. This membrane is able to achieve high rejection rates because of the small pores.

Membrane 10: Although this membrane showed relatively small pores which are relatively further apart the extreme hydrophilic character helps more water to pass through per unit area of the membrane. But the faster the water passes through gives the membrane a lower opportunity to hold on to the protein particles.

Viscosity of the casting solution:

The viscosity of the solution helps determine the tensile strength and stability of the membrane.

Table 10: Viscosity of the membranes

EXP #	Viscosity (cP)	Flux (L/m^2.hr)	Rejection (%)
1	175600	443.808	6.81
2	38578	89.1	52.12
3	251.24	2164.32	9.3
4	2558	5388.66	0.83
5	20520	4026.708	5.08
6	4540	1203.12	8.59
7	1067.6	534.672	30.45
8	128920	142.38	72.57
9	13550	214.776	70.35
10	1327.25	889.272	34.31

The higher the viscosity of a certain casting solution means that the membrane produced will be more stable and will be less prone to breakage. But too high of a viscosity means that the membranes is hard to scrape because of rubbery characteristics. It was extremely difficult to produce membranes 1, 2, 5, and 8 because of this particular reason. Membrane 3 was very difficult to move around for testing because of its weak tensile strength resulting from the low viscosity of the casting solution.

Porosity of the membranes:

The porosity of the membrane helps determine the void fraction of the membrane and is a direct determinant of the flux of the membrane.

Table 11: Porosity of the membranes

EXP #	Porosity (%)	Flux (L/m^2.hr)	CA degrees
1	23.74	443.808	72
2	43.02	89.1	78
3	6.37	2164.32	75
4	24.53	5388.66	70
5	16.9	4026.708	81
6	12.82	1203.12	91
7	36.84	534.672	72
8	26.76	142.38	82
9	53.95	214.776	83
10	95.94	889.272	69

The porosity and hydrophilicity of the membrane can be used to determine the flux of the membrane. Even though a membrane is highly porous and is expected to have a high flux the amount of hydrophilicity/hydrophobicity is a barrier to that.

Flux and Rejection:

The direct analysis method using responses of flux and rejection can be used to judge the membrane with the best performance. 5 out of the 10 membrane that were prepared were already chosen to run AFM experiment. These were chosen according to good balance between flux and rejection and a high enough tensile strength to hold the membrane together while water and other components are passing through it.

Table 12: Relation between flux, Rejection and the characteristics

EXP #	Flux (L/m^2.hr)	Rejection (%)
1	443.808	6.81
2	89.1	52.12
3	2164.32	9.3
4	5388.66	0.83
5	4026.708	5.08
6	1203.12	8.59
7	534.672	30.45
8	142.38	72.57
9	214.776	70.35
10	889.272	34.31

The most ideal membrane would have a fair balance between flux and rejection. A very high rejection would mean a fairly low flux while a fairly high flux would mean that not all particles are being properly separated. The most noteworthy of the all the membranes designed is that of membrane 8, 9 and 10. Although membrane 8 and 9 has fairly high rejection, the flux is fairly low. Despite this fact it is highly recommended for industrial use for high separation quality. Membrane 10 has a very high flux most appropriate for large scale processes and the rejection would be much higher if it were separating larger particles.

Membranes 2 and 7 were with fair rejection and flux rates respectively, are not recommended for large scale use because of either poor separation quality or poor economic benefits. The rest of the membranes were either prone to breakage or as it can be seen in the above table the flux to rejection balance was very poor for further consideration.

Optimization using linear regression:

The uniform design method was mainly used for optimization purposes from the responses found from the fixed experiments. In order to do this a statistical software PASW Statistics v17, IBM was used. Through backward regression method this software is able to detect the most significant variables that affect the responses of the experiment. The results of the backward regression from PASW statistics is illustrated in Appendix D. The regression resulted in a certain expressions consisting of the variables and coefficients which predict response values if different variable values were used.

The two linear regression model expressions were:

$$Flux: \;\; Y1 = 7818.648 - 36.313X1 - 57.297X2 + 1003.502$$

$$Rejection: \;\; Y2 = \; -91.855 + 1.202X1 + 0.797X2 - 1.825X4$$

$$\text{Where, } Y1 \rightarrow Response\ prediction\ of\ Flux$$

$$Y2 \rightarrow Response\ prediction\ of\ rejection$$

$$X1 \rightarrow Bath\ temperature\ of\ casting\ solution$$

$$X2 \rightarrow Blend\ ratio$$

$$X4 \rightarrow Weight\ \%\ of\ Additive$$

The regression plots are illustrated in Appendix C.

These plots help predict the combination that is needed to produce a membrane with the best performance, meaning an appropriate balance between flux and rejection.

According to the plots and optimization analysis the following results were achieved for predicted membrane combinations:

Table 13: Combination for producing optimized membranes.

Membrane	Additive	Weight % Additive	Bath Temperature	Blend Ratio	Flux	Rejection
A	PEG 1000, LiCl	1	40	90	1210.028	26.13
B	PEG 600, LiCl	1	80	80	330.408	66.24
C	PVP,Ca(NO3)2	1	100	10	3614.448	34.49
D	PEG 600, PVP	10	50	100	187.608	83.98675

Conclusions:

According to all the characterizations and performance evaluations performed on all the membranes it is evident that membranes 2,7,8,9 and 10 are the ones with the best performance. The performances of the membranes are judged on their balance between flux and rejection. Each membrane was tested for viscosity, surface roughness, pore depths, pore separation, functional group and hydrophilicity. Based on the results quantified in tables 10, 11 and 12 it can be seen:

- Membrane 2: The viscosity of the casting is fairly high which counts for the stable tensile strength that this membrane possesses. Although the porosity is high this membrane has a relatively low flux and a very high rejection rate. This could be a result of the complexes of Li^+ formed on the surface of the membrane which prohibits large amounts of water molecules to pass through. On the other hand these complexes also helps reject a lot of the protein molecules trying to pass through it. Despite the high rejection value, the low flux does not allow this membrane to be used in large industrial applications for poor economic benefits.
- Membrane 7: With a fairly high tensile strength this membrane proved to be a one of the more reliable ones. According to its porosity it does have a fairly high flux but in turn a fairly poor rejection rate. The rejection rate could be higher if larger sized proteins were used for percentage retentate testing. This leaves membrane 7. Hence membrane 7 is apt for industrial applications for greater economic advantages.
- Membrane 8: This membrane was produced with a novelty additive of $CaNO_3$ and proved to be more apt at rejecting protein than any of the other membranes. This can be recommended for large scale applications only if the use calls for high quality separations.
- Membrane 9: With relatively higher porosity and hence relatively higher flux this membrane has equal rejection capabilities as membrane 8 and hence would be more cost effective compared to membrane 8.
- Membrane 10: This membrane is the most hydrophilic according to the CA tests run on it. This hydrophilicity also accounts for the large flux capabilities that this membrane holds. Given a situation of rejecting larger protein molecules in this membrane would be able to do it most cost effectively. Hence, this membrane is highly recommended for large scale industrial applications.

According to the optimization process it can be seen that additives like LiCl and $CaNO_3$ in small amounts improves the functionality of the membrane. On the other hand additives like PVP and PEG 600 work better at higher compositions. Finally, using the statistical optimization method proved to be an extremely efficient way of determining the combinations for producing a membrane with even better capabilities.

- Membrane A: This membrane should contain low amounts of PEG-1000 and LiCl additives. With a combination of low bath temperature and high amounts of PVC this membrane could prove to be extremely cost effective owing to its high flux value. But on the other hand it is recommended for the rejection of larger protein molecules.
- Membrane B: PEG-600 and LiCl in low amounts should be used to produce this membrane. With a high bath temperature and relatively high blend ratio this membrane proves to have excellent rejection qualities and also fairly high flux making it extremely favorable for industrial applications.
- Membrane C: with low amounts of calcium nitrate and PVP this membrane shows excellent rejection quality for larger protein molecules and one of the highest flux values. This membrane would be extremely cost effective for large scale processes.
- Membrane D: This membrane has one the highest rejection rates with a fairly low flux and hence is very appropriate for large scale high purification processes.

It can be recommended to use this method with other variables like solvent characteristics, coagulation bath temperatures, protein molecular weight and so forth to engineer a much more efficient membrane with higher flux and rejection values.

Recommendations:

There are many ways by which this experimental process could be improved. The following points are recommended for future investigations in this topic:

1) It is evident that more factors and levels of an experimental design method will help attain better results. Hence, it is very important that the number of factors and more importantly the number of levels be increased for more accurate predictions for optimization.
2) As mentioned above, the factors or variables used could be increased and things like solvent characteristics, coagulation bath temperatures, protein molecular weight and so forth would help find more accurate dependence of the responses on the independent variables.
3) The machines used for characterization should must be functional and clean before use.
4) It is extremely important to let the casting solution mix completely before it is scraped.
5) The protein rejection studies depend highly on the size of the protein being used. The used of heavier or larger protein particles would have helped achieve higher rejection rates and better results.
6) Membrane performance can be exceedingly hampered by dust particles that deposit on the surface if the membrane is left outside in the open air. Proper storage of the membrane is highly recommended.

Appendix A:

Factorial Design Tables: [19]

Table 14: Column selection for Table 3

The number of factors	The number of the column to be selected									
2	1	7								
3	1	5	7							
4	1	2	5	7						
5	**1**	**2**	**3**	**5**	**7**					
6	1	2	3	5	7	10				
7	1	2	3	4	5	7	10			
8	1	2	3	4	5	6	7	10		
9	1	2	3	4	5	6	7	9	10	
10	1	2	3	4	5	6	7	8	9	10

Table 15: U11 (11^10): Defines the design combination

EXPERIMENT	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
1	**1**	**2**	**3**	4	**5**	6	**7**	8	9	10
2	**2**	**4**	**6**	8	**10**	1	**3**	5	7	9
3	**3**	**6**	**9**	1	**4**	7	**10**	2	5	8
4	**4**	**8**	**1**	5	**9**	2	**6**	10	3	7
5	**5**	**10**	**4**	9	**3**	8	**2**	7	1	6
6	**6**	**1**	**7**	2	**8**	3	**9**	4	10	5
7	**7**	**3**	**10**	6	**2**	9	**5**	1	8	4
8	**8**	**5**	**2**	10	**7**	4	**1**	9	6	3
9	**9**	**7**	**5**	3	**1**	10	**8**	6	4	2
10	**10**	**9**	**8**	7	**6**	5	**4**	3	2	1
11	**11**	**11**	**11**	11	**11**	11	**11**	11	11	11

Table 16: Numerical statistical combination

Experiment	Temperature of bath (A)	PVC/xxx (Blend Ratio)(B)	Wt.% of Polymer(C)	Additive (D)	Wt.% of Additive. (E)
1	1	2	3	5	7
2	2	4	6	10	3
3	3	6	9	4	10
4	4	8	1	9	6
5	5	10	4	3	2
6	6	1	7	8	9
7	7	3	10	2	5
8	8	5	2	7	1
9	9	7	5	1	8
10	10	9	8	6	4

Table 17: Defining the levels and factors

Levels\Factors	Temperature of bath (A)	PVC/xxx (Blend Ratio)(B)	Wt.% of Polymer(C)	Additive (D)	Wt. % of Additive. (E)
1	40	9:1	25	PEG 600	1
2	50	8:2	20	PEG 1000	3
3	60	7:3	18	PVP	5
4	70	6:4	15	FeCl2	7
5	80	5:5	10	LiCl	10

Table 18: Factor and Level correlation matrix

Experiment	Temperature of bath (A)	PVC/xxx (Blend Ratio)(B)	Wt.% of Polymer(C)	Additive (D)	Wt. % of Additive. (E)
1	A1	B1	C1	D1	E1
2	A1	B1	C1	D1	E1
3	A2	B2	C2	D2	E2
4	A2	B2	C2	D2	E2
5	A3	B3	C3	D3	E3
6	A3	B3	C3	D3	E3
7	A4	B4	C4	D4	E4
8	A4	B4	C4	D4	E4
9	A5	B5	C5	D5	E5
10	A5	B5	C5	D5	E5

Table 19: Final combination according to statistical combination

Experiment	Temperature of bath (A)	PVC/xxx (Blend Ratio)(B)	Wt.% of Polymer(C)	Additive (D)	Wt. % of Additive. (E)
1	A1	B1	C2	D3	E4
2	A1	B2	C3	D5	E2
3	A2	B3	C5	D2	E5
4	A2	B4	C1	D5	E3
5	A3	B5	C2	D2	E1
6	A3	B1	C4	D4	E5
7	A4	B2	C5	D1	E3
8	A4	B3	C1	D4	E1
9	A5	B4	C3	D1	E4
10	A5	B5	C4	D3	E2

Table 20: Final Design combination

Experiment	Temperature of bath (A)	PVC/xxx (Blend Ratio)(B)	Wt.% of Polymer(C)	Additive (D)	Wt. % of Additive. (E)
1	40	9:1	20	PVP	7
2	40	8:2	18	LiCl	3
3	50	7:3	10	PEG 1000	10
4	50	6:4	21	LiCl	5
5	60	5:5	20	PEG 1000	1
6	60	9:1	15	CaNO3	10
7	70	8:2	10	PEG 600	5
8	70	7:3	21	CaNO3	1
9	80	6:4	18	PEG 600	7
10	80	5:5	15	PVP	3

Appendix B:

Sample Calculations:

Determination of polymer and additive amounts:

$$\frac{x}{x+y+z} = \boldsymbol{Wp}$$ Equation 4

$$\frac{y}{x+y+z} = \boldsymbol{Wa}$$ Equation 5

Here, x = amount of PVC +PVB

y=amount of additive

z = amount of DMAc

Wp = weight % of polymer

Wa = weight % of additive

Eq. 4 and 5 can be rewritten as:

$$(1 - Wp)x - Wpy = Wp * z$$

$$(1 - Wa)y - Wax = Wa * z$$

Using this and given values of Wp, Wa and z values of x and y can be found.

The excel formula MMULT (MINVERSE (Array1) (Array2)) can solve for values of x and y automatically as a simultaneous equation.

Porosity of membrane:

Porosity of the membrane is calculated using equation 1:

$$\boldsymbol{Porosity} = \frac{(\boldsymbol{W2}) - (\boldsymbol{W1})}{\boldsymbol{\rho met} * \boldsymbol{Vm}}$$

For membrane 1:

$$\boldsymbol{Porosity} = \frac{(\mathbf{0.2693}) - (\mathbf{0.0615})}{\mathbf{0.9989} * \mathbf{5.8} * \mathbf{4.5} * \mathbf{0.019}} = 41.7\%$$

Pure water flux of the membrane:

The pure water flux can be found by using equation 2:

$$\boldsymbol{Flux, Jw = \frac{V}{A * t}}$$

For membrane 1:

$$\boldsymbol{Flux, Jw} = \frac{\boldsymbol{276.2\ ml}}{\boldsymbol{0.003473\ m^2} * 753\ s} = 105.614\frac{ml}{m^2.s}$$

Rejection of membrane:

The rejection of the membrane can be found using equation 3:

$$\boldsymbol{Rejection = \left(1 - \left(\frac{Cp}{Cf}\right)\right) * 100}$$

For membrane 1: (Cp and Cf from correlation given in graph 1)

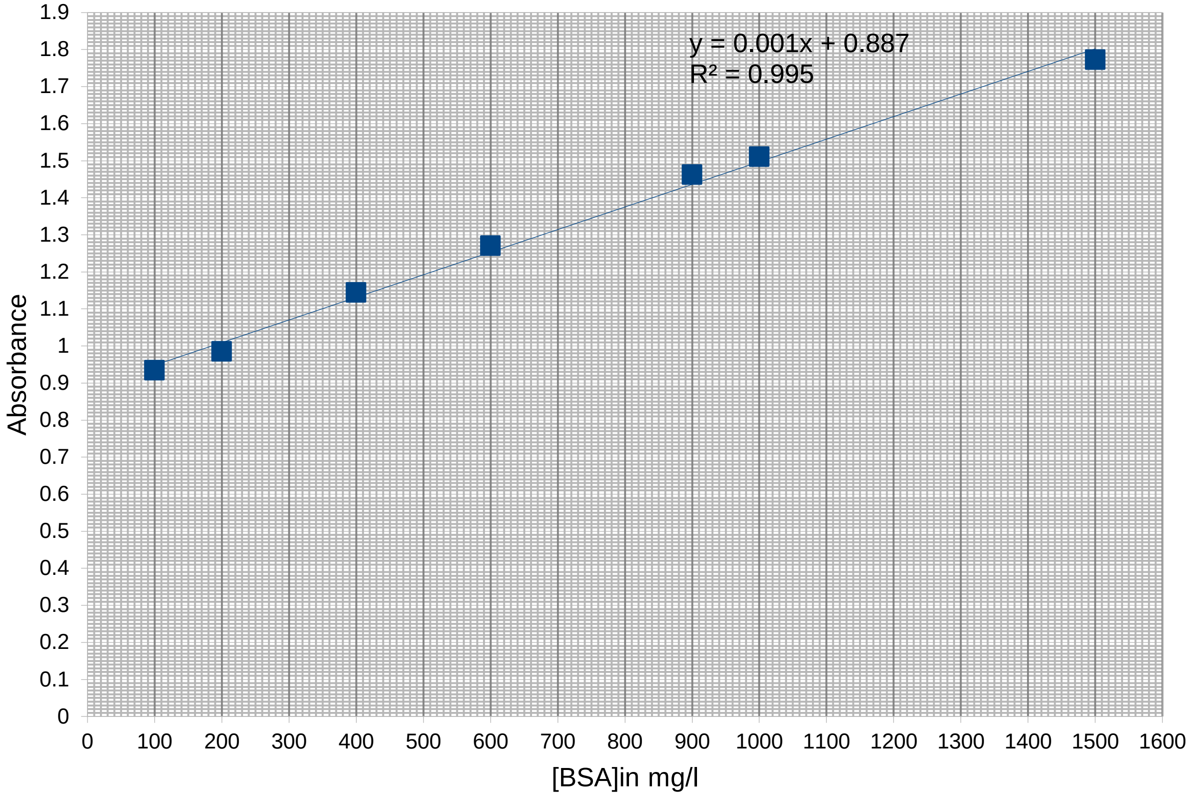
$$\boldsymbol{Rejection = \left(1 - \left(\frac{945}{1020}\right)\right) * 100} \ = \ 7.35\%$$

Appendix C:

Graphs:

Table 21: Absorbance and concentration relation

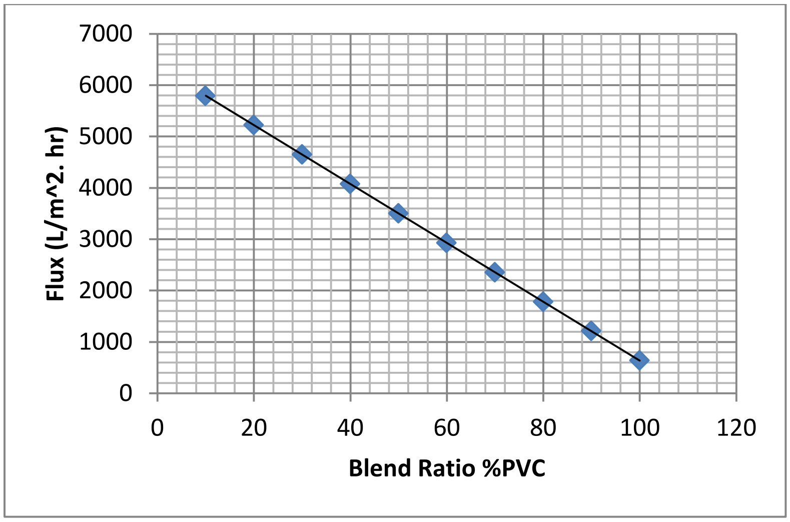
[BSA]	Absorbance
100	0.934
200	0.985
400	1.144
600	1.27
900	1.462
1000	1.51
1500	1.772



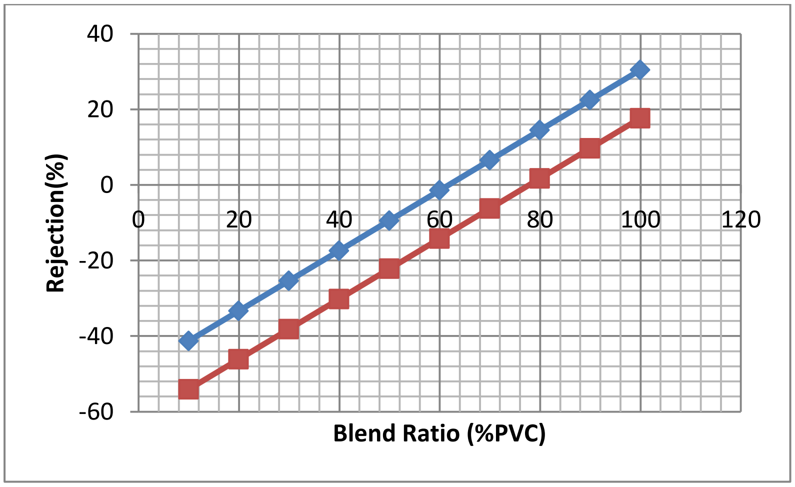
Graph 1: Absorbance and Concentration determination (Reference absorbance calibration).

Table 22: Flux and rejection variance according to blend ratio with bath temp at 40

Regression Flux Equation	Regression Rej. Equation	Bath Temperature	Blend Ratio	Weight % Additive	Weight % Additive	Rej.
5793.228	-41.28	40	10	3	10	-54.055
5220.328	-33.31		20			-46.085
4647.428	-25.34		30			-38.115
4074.528	-17.37		40			-30.145
3501.628	-9.4		50			-22.175
2928.728	-1.43		60			-14.205
2355.828	6.54		70			-6.235
1782.928	14.51		80			1.735
1210.028	22.48		90			9.705
637.128	30.45		100			17.675



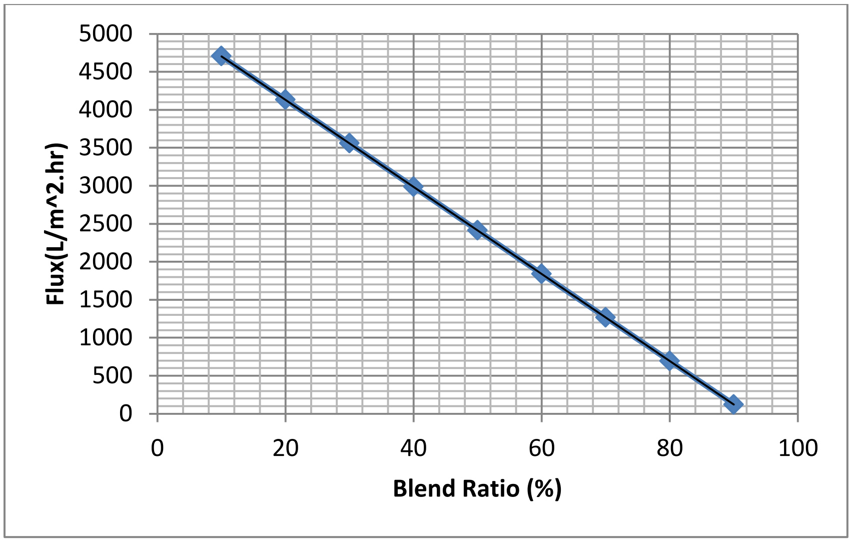
Graph 2: Flux against Blend ratio at bath temperature of 40



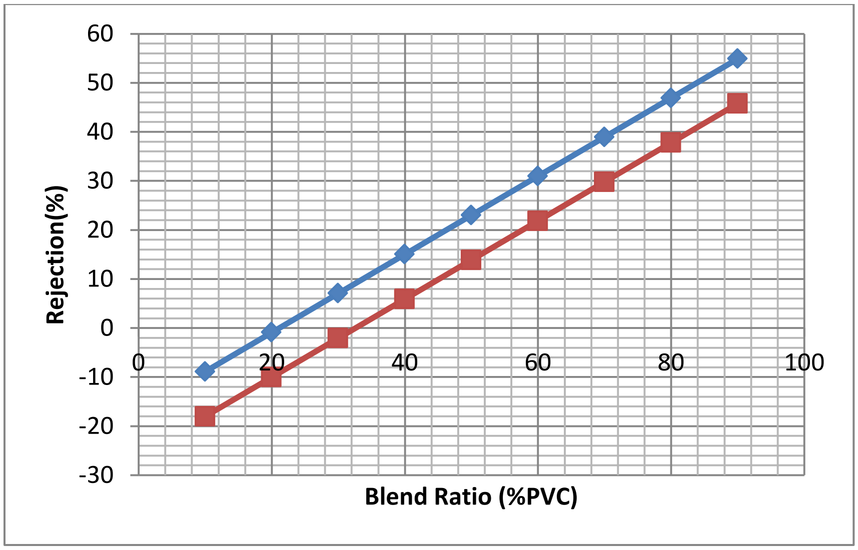
Graph 3: Rejection against blend ratio at bath temperature of 4

Table 23: Flux and rejection variance according to blend ratio with bath temp at 70

Regression Flux Equation	Regression Rej. Equation	Bath Temperature	Blend Ratio	Weight % Additive	Weight % Additive	Rej
4703.838	-8.87	70	10	5	10	-17.995
4130.938	-0.9		20			-10.025
3558.038	7.07		30			-2.055
2985.138	15.04		40			5.915
2412.238	23.01		50			13.885
1839.338	30.98		60			21.855
1266.438	38.95		70			29.825
693.538	46.92		80			37.795
120.638	54.89		90			45.765



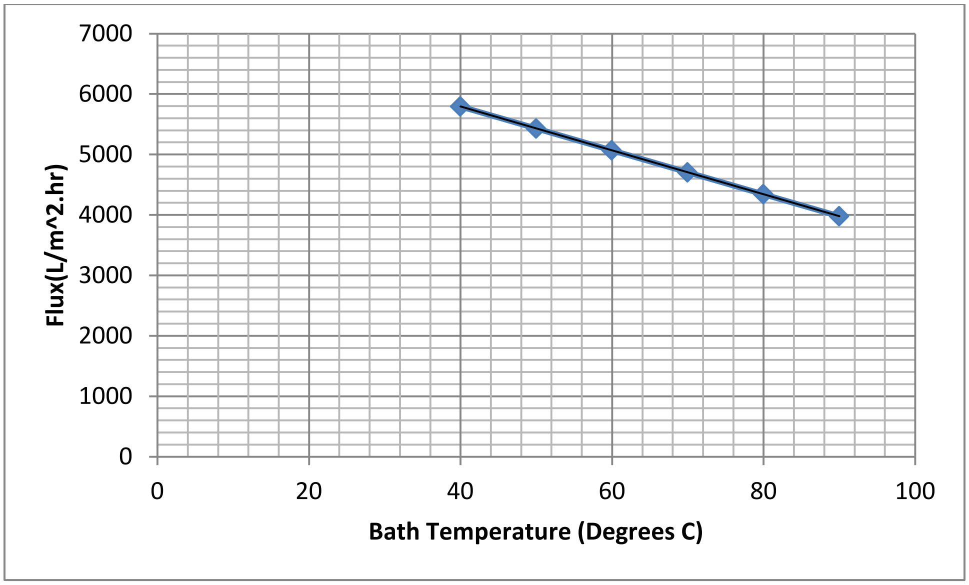
Graph 4: Flux against blend ratio at bath temp of 70



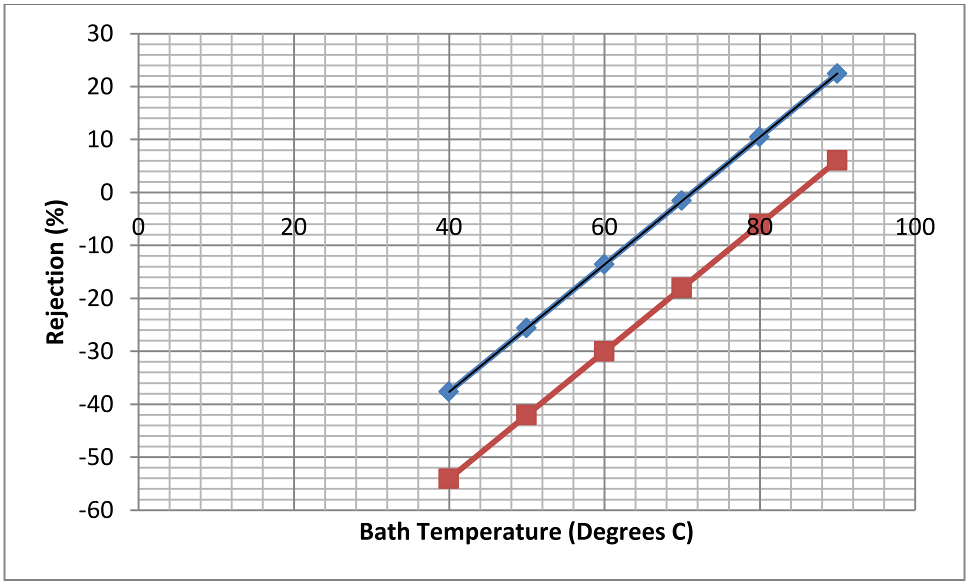
Graph 5: Rejection against blend ratio at bath temp of 70

Table 24: Flux and rejection variance according to bath temp with blend ratio at 10.

Regression Flux Equation	Regression Rej. Equation	Bath Temperature	Blend Ratio	Weight % Additive	Weight % Addtive	Rej.
5793.228	-37.63	40	10	1	10	-54.055
5430.098	-25.61	50				-42.035
5066.968	-13.59	60				-30.015
4703.838	-1.57	70				-17.995
4340.708	10.45	80				-5.975
3977.578	22.47	90				6.045



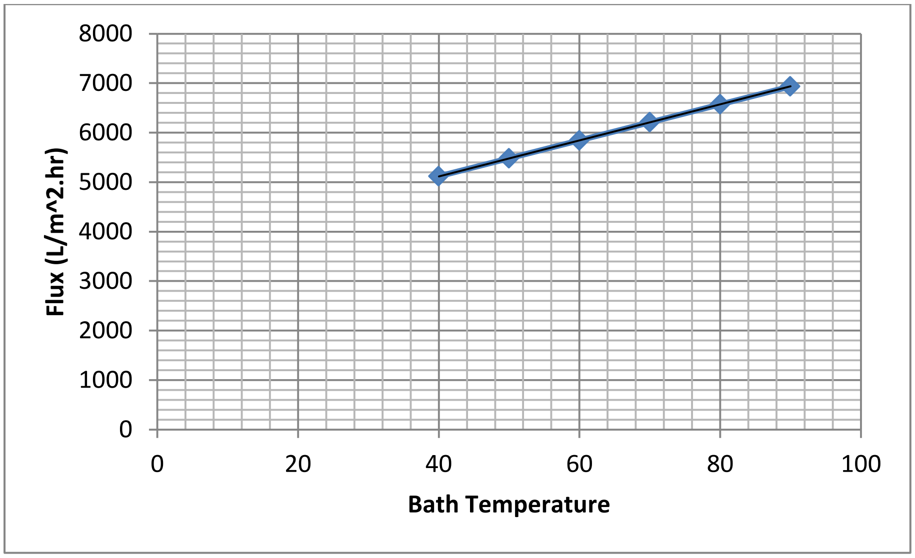
Graph 6: Flux against bath temp at blend ratio of 10



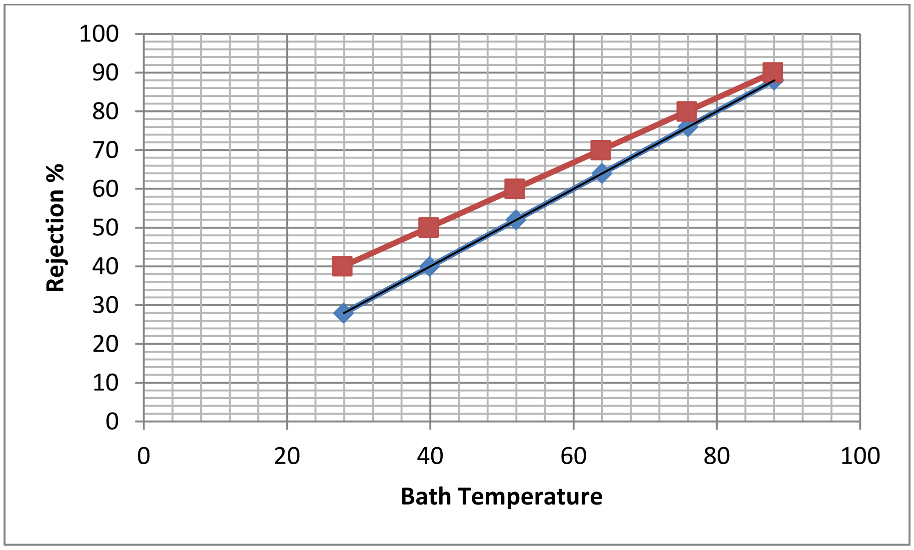
Graph 7: Rejection against bath temp at blend ratio of 10

Table 25: Flux and rejection variance according to bath temp with blend ratio at 90.

Regression Flux Equation	Regression Rej. Equation	Bath Temperature	Blend Ratio	Weight % Additive	Weight % Addtive	Rej.
5118.57	27.93675	40	90	1%	10%	27.7725
5481.7	39.95675	50				39.7925
5844.83	51.97675	60				51.8125
6207.96	63.99675	70				63.8325
6571.09	76.01675	80				75.8525
6934.22	88.03675	90				87.8725

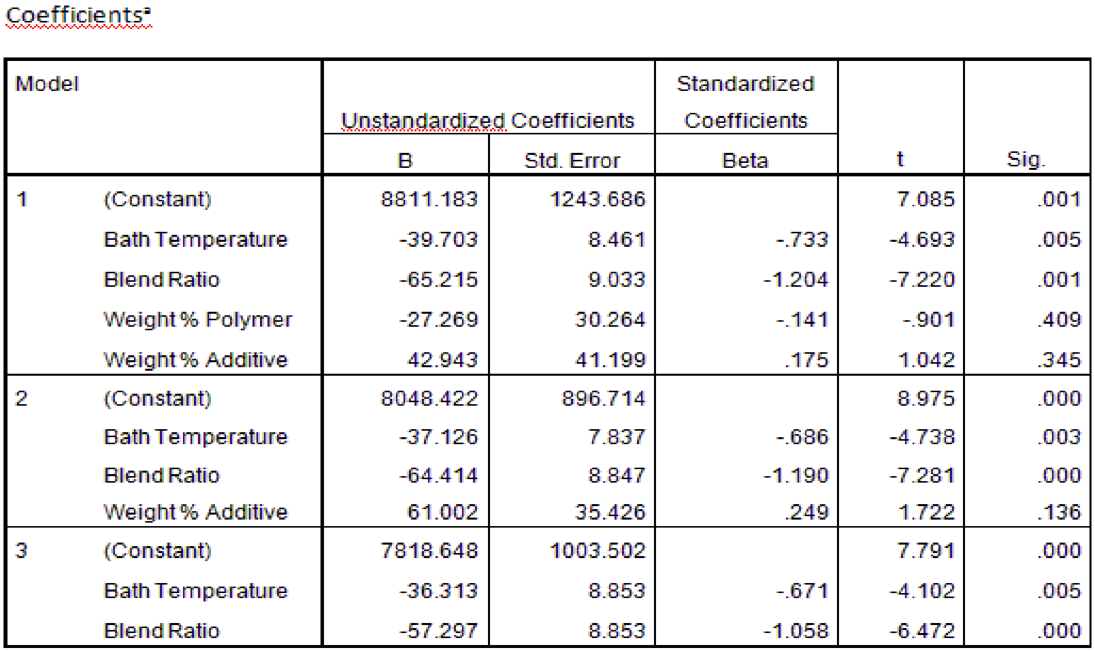


Graph 8: Flux against bath temp at blend ratio of 90.



Graph 9: Rejection against bath temp at blend ratio of 90.

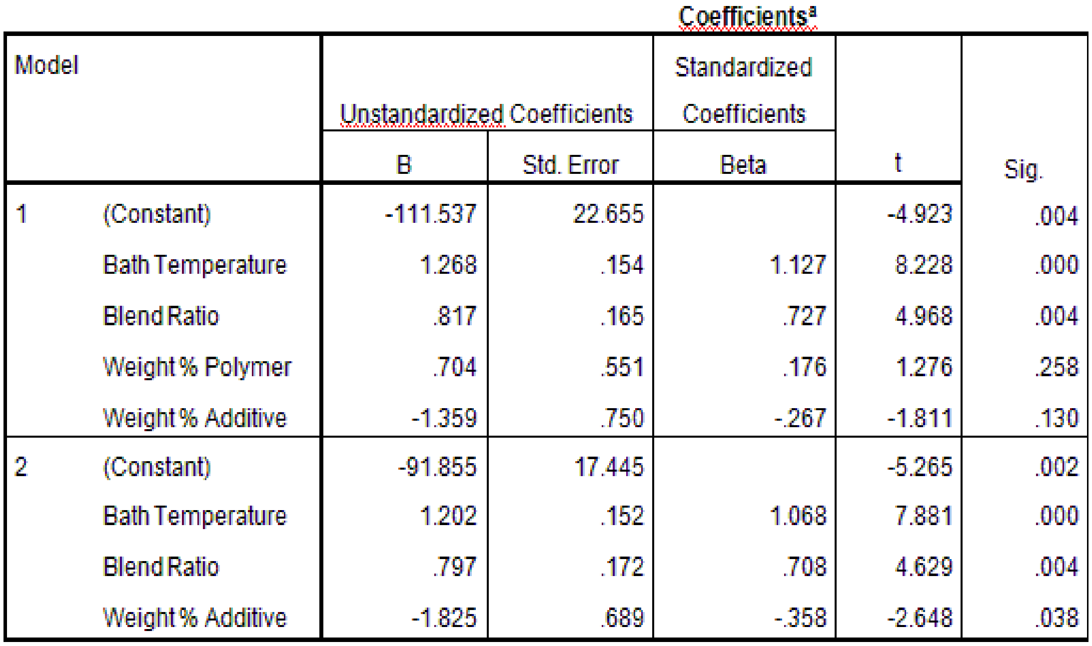
Appendix D:



Coefficients^a

Model		Unstandardized Coefficients		Standardized Coefficients	t	Sig.
		B	Std. Error	Beta		
1	(Constant)	8811.183	1243.686		7.085	.001
	Bath Temperature	-39.703	8.461	-.733	-4.693	.005
	Blend Ratio	-65.215	9.033	-1.204	-7.220	.001
	Weight % Polymer	-27.269	30.264	-.141	-.901	.409
	Weight % Additive	42.943	41.199	.175	1.042	.345
2	(Constant)	8048.422	896.714		8.975	.000
	Bath Temperature	-37.126	7.837	-.686	-4.738	.003
	Blend Ratio	-64.414	8.847	-1.190	-7.281	.000
	Weight % Additive	61.002	35.426	.249	1.722	.136
3	(Constant)	7818.648	1003.502		7.791	.000
	Bath Temperature	-36.313	8.853	-.671	-4.102	.005
	Blend Ratio	-57.297	8.853	-1.058	-6.472	.000

Figure 26: Backward regression on Flux



Coefficients^a

Model		Unstandardized Coefficients		Standardized Coefficients	t	Sig.
		B	Std. Error	Beta		
1	(Constant)	-111.537	22.655		-4.923	.004
	Bath Temperature	1.268	.154	1.127	8.228	.000
	Blend Ratio	.817	.165	.727	4.968	.004
	Weight % Polymer	.704	.551	.176	1.276	.258
	Weight % Additive	-1.359	.750	-.267	-1.811	.130
2	(Constant)	-91.855	17.445		-5.265	.002
	Bath Temperature	1.202	.152	1.068	7.881	.000
	Blend Ratio	.797	.172	.708	4.629	.004
	Weight % Additive	-1.825	.689	-.358	-2.648	.038

Figure 27: Backward regression on Rejection

Appendix E:

Raw data tables:

Porosity of Membranes:

Table 26: Raw Data for Porosity

Membrane	1	1	1	2	2	2
Length	5.8			7.3		
Breadth	4.5	1.95	1.95	4.6	1.95	1.95
Thickness	0.019	0.011	0.011	0.008	0.031	0.009
Volume of the film	0.4991625	0.0328555	0.0328555	0.2560475	0.09259278	0.02688177
Room Temperature	16	18	18	16	18	18
Density of Water	0.9989	0.9989	0.9989	0.9989	0.9989	0.9989
Weight of Wet Membrane w1 (g)	0.2693	0.0146	0.0148	0.1304	0.1228	0.0175
Weight of Dry Membrane w2 (g)	0.0615	0.0107	0.0090	0.0747	0.0408	0.0125
Porosity of membrane	41.673779	11.8832298	17.6724956	21.7767942	88.6573474	18.6204456
Average Porosity		23.74316815			43.01819575	

Membrane	3	3	3	4	4	4
Length	5.1			5.7		
Breadth	4.8	1.95	1.95	4.3	1.95	1.95
Thickness	0.013	0.013	0.041	0.013	0.015	0.013
Volume of the film	0.31824	0.03882923	0.12246141	0.31863	0.04480296	0.03882923
Room Temperature	16	18	18	16	18	18
Density of Water	0.9989	0.9989	0.9989	0.9989	0.9989	0.9989
Weight of Wet Membrane w1	0.0699	0.0411	0.0192	0.1001	0.0276	0.0276
Weight of Dry Membrane w2	0.0497	0.0184	0.0114	0.0399	0.0164	0.0161
Porosity of membrane	6.35412707	58.5254929	6.37636722	18.9133788	25.0258789	29.6494788
Average Porosity		6.365247148			24.5295788	

Membrane	5	5	5	6	6	6
Length	4.9			5.15		
Breadth	4.15	1.95	1.95	3.15	1.95	1.95
Thickness	0.014	0.018	0.012	0.023		
Volume of the film	0.2745225	0.05376355	0.03584237	0.3731175		
Room Temperature	16	18	18	16	18	18
Density of Water	0.9989	0.9989	0.9989	0.9989	0.9989	0.9989
Weight of Wet Membrane w1	0.1013	0.0301	0.0187	0.1239		
Weight of Dry Membrane w2	0.0613	0.0200	0.0125	0.0761		
Porosity of membrane	14.5861723	18.8066501	17.3170144	12.8245333		
Average Porosity		16.9032789				

Membrane	7	7	7	8	8	8
Length	4.5			4.35		
Breadth	3.9	1.95	1.95	4.3	1.95	1.95
Thickness	0.023	0.026	0.061	0.012	0.013	0.013
Volume of the film	0.394875	0.07765846	0.18219869	0.21978375	0.03882923	0.03882923
Room Temperature	16	18	18	16	18	18
Density of Water	0.9989	0.9989	0.9989	0.9989	0.9989	0.9989
Weight of Wet Membrane w1	0.2110	0.0741	0.0431	0.1014	0.0342	0.0294
Weight of Dry Membrane w2	0.0562	0.0304	0.0159	0.0638	0.0196	0.0195
Porosity of membrane	39.2437599	56.3340096	14.945197	17.1258272	37.6419469	25.5243339
Average Porosity		36.8409888			26.764036	

Membrane	9	9	9	10	10	10
Length	4.85			4.7		
Breadth	3.9	1.95	1.95	3.9	1.95	1.95
Thickness	0.029	0.030	0.011	0.011	0.013	0.013
Volume of the film	0.54380625	0.08960591	0.0328555	0.2062125	0.03882923	0.03882923
Room Temperature	16	18	18	16	18	18
Density of Water	0.9989	0.9989	0.9989	0.9989	0.9989	0.9989
Weight of Wet Membrane w1	0.5041	0.1059	0.0197	0.2216	0.0489	0.0524
Weight of Dry Membrane w2	0.1524	0.0348	0.0139	0.0382	0.013	0.0112
Porosity of membrane	64.7422019	79.4348209	17.6724956	89.0314888	92.557938	106.22248
Average Porosity		53.9498395			95.9373024	

Viscosity of casting solution:

Table 27: Raw Data for Viscosity

Viscosity of Casting Solution	1	2	2	2	2	2
Solution Temperature	16.5	17	18	18	18	18
Rotor Model	64	64	64	64	64	64
Sample Volume (ml)	100	100	100	100	100	100
Velocity (RPM)	3	20	12	10	6	5
Torque (%)	87.8	90.9	68.4	61.2	45.9	41.1
Viscosity (cP)	175600	27330	34200	36660	45700	49000
Average Viscosity				38578		

Viscosity of Casting Solution	3	3	3	3	3	4	4	4	4	4
Solution Temperature	17	17	18	18	18	17	17	17	17	17
Rotor Model	62	62	62	62	62	63	63	63	63	63
Sample Volume (ml)	100	100	100	100	100	100	100	100	100	100
Velocity (RPM)	100	60	50	30	20	30	20	12	10	6
Torque (%)	84.2	50.6	42.4	25.2	16.4	65	42.1	25.4	21.5	12.7
Viscosity (cP)	252.9	252.5	253.8	252	245	2612	2538	2540	2580	2520
Average Vis.			251.24					2558		

Viscosity of Casting Solution	**5**	**6**	**7**	**7**	**7**	**7**	**7**
Solution Temperature	17	30	17	18	18	18	18
Rotor Model	64	64	62	62	62	62	62
Sample Volume (ml)	50	100	100	100	100	100	100
Velocity (RPM)	20	50	100	60	50	30	20
Torque (%)	68.4	37.8	90.8	53.9	44.9	26.6	17.2
Viscosity (cP)	20520	4540	1088	1076	1078	1064	1032
Average Viscosity			1067.6				

Viscosity of Casting Solution	**8**	**8**	**8**	**8**	**8**
Solution Temperature	17	18	18	18	18
Rotor Model	64	64	64	64	64
Sample Volume (ml)	100	100	100	100	100
Velocity (RPM)	5	4	3	2.5	2
Torque (%)	89.2	76.3	60.9	59.3	53.1
Viscosity (cP)	107500	114500	122400	140900	159300
Average Viscosity	128920				

Viscosity of Casting Solution	**9**	**9**	**9**	**9**	**9**
Solution Temperature	70	70	70	70	70
Rotor Model	64	64	64	64	64
Sample Volume (ml)	100	100	100	100	100
Velocity (RPM)	50	30	20	12	10
Torque (%)	59.4	68.3	56.3	32.1	27.6
Viscosity (cP)	6820	12000	16740	16050	16140
Average Viscosity	13550				

Viscosity of Casting Solution	10	10	10	10
Solution Temperature	17	18	18	18
Rotor Model	62	62	62	62
Sample Volume (ml)	100	100	100	100
Velocity (RPM)	20	12	10	6
Torque (%)	89.2	53.3	44.3	26.2
Viscosity (cP)	1337	1333	1329	1310
Average Viscosity	1327.25			

Flux:

Table 28: Raw Data for flux

Pure Water Flux of the membrane	1	1	1	2	2	2
Temperature of water	18	18	18	17	17	17
Membrane Area (m^2)	0.003473	0.003473	0.003473	0.003473	0.003473	0.003473
Pre-Pressure	0.12	0.12	0.12	0.12	0.12	0.12
Time for Pre-Pressure	0.5	0.5	0.5	0.5	0.5	0.5
Operation Pressure	0.1	0.1	0.1	0.1	0.1	0.1
Volume of filtered DI water	276.2	297.7	18.6	307.4	32.9	10.7
Time for Filtration	753	3074	38	1632	915	319
Flux (Jw = V/A.t) in ml/m^2.s	105.614589	27.8849704	140.936851	54.2349102	10.3530907	9.65802469
Average Flux		123.27572			24.7486752	

Pure Water Flux of the membrane	3	3	3	4	4	4
Temperature of water	17	18	18	18	18	18
Membrane Area (m^2)	0.003473	0.003473	0.003473	0.003473	0.003473	0.003473
Pre-Pressure	0.12	0.12	0.12	0.12	0.12	0.12
Time for Pre-Pressure	0.5	0.5	0.5	0.5	0.5	0.5
Operation Pressure	0.1	0.1	0.1	0.1	0.1	0.1
Volume of filtered DI water	274.3	16.9	311.4	206	190.7	313.6
Time for Filtration	78	66	125	41	42	52
Flux (Jw = V/A.t) in ml/m^2.s	1012.57318	73.7289393	717.304924	1446.70033	1307.36429	1736.47257
Average Flux		601.202349			1496.84573	

Pure Water Flux of the membrane	5	5	5	7	7
Temperature of water	17	16	18	18	17
Membrane Area (m^2)	0.003473	0.003473	0.003473	0.003473	0.003473
Pre-Pressure	0.12	0.12	0.12	0.12	0.12
Time for Pre-Pressure	0.5	0.5	0.5	0.5	0.5
Operation Pressure	0.1	0.1	0.1	0.1	0.1
Volume of filtered DI water	310.8	246.7	22.6	291.7	300
Time for Filtration	82	62	19	594	555
Flux (Jw = V/A.t) in ml/m^2.s	1091.34578	1145.70465	342.491703	141.39863	155.640812
Average Flux		1118.52522			148.519721

Pure Water Flux of the membrane	8	8	9	9	10	10
Temperature of water	18	17	18	17	17	18
Membrane Area (m^2)	0.003473	0.003473	0.003473	0.003473	0.003473	0.003473
Pre-Pressure	0.12	0.12	0.12	0.12	0.12	0.12
Time for Pre-Pressure	0.5	0.5	0.5	0.5	0.5	0.5
Operation Pressure	0.1	0.1	0.1	0.1	0.1	0.1
Volume of filtered DI water	306.4	9.3	266	301	254.1	28.3
Time for Filtration	1200	480	1452	1302	252	40
Flux (Jw = V/A.t) in ml/m^2.s	73.5195316	5.57875036	52.7485149	66.5657344	290.334965	203.714368
Average Flux		39.549141		59.6571247		247.024666

Rejection:

Table 29: Raw Data for rejection

Rejection	1	1	1	2	2	2
Concentration for BSA	1020	1127	1035	1020	1200	1180
Volume of PBS buffer	30	30	30	30	30	30
Operation Pressure	0.1	0.1	0.1	0.1	0.1	0.1
Absorbance of Raw water	1.5060	1.5750	1.5150	1.5060	1.6190	1.6070
Absorbance of Filtered water	1.4640	1.5300	1.4760	1.1870	1.2430	1.2330
Concentration of Raw water	1020	1127	1035	1020	1200	1180
Concentration of Filtrate	945	1056	965	490	587	551
R= (1- Cp/Cf)*100	7.35294118	6.29991127	6.76328502	51.9607843	51.0833333	53.3050847
Average Rejection		6.805379			52.11640	

Rejection	3	3	4	4	5	5
Concentration for BSA	1085	1160	1048	1115	995	1130
Volume of PBS buffer	30	30	30	30	30	30
Operation Pressure	0.1	0.1	0.1	0.1	0.1	0.1
Absorbance of Raw water	1.5450	1.5960	1.5220	1.5660	1.4940	1.5750
Absorbance of Filtered water	1.4930	1.5190	1.5200	1.5600	1.4700	1.5290
Concentration of Raw water	1085	1160	1048	1115	995	1130
Concentration of Filtrate	1000	1035	1040	1105	960	1055
R= (1- Cp/Cf)*100	7.83410138	10.7758621	0.76335878	0.89686099	3.51758794	6.63716814
Average Rejection		9.30498173		0.83010988		5.07737804

Rejection	7	7	8	8	9	9	10	10
Concentration for BSA	1100	1082	1030	1000	1018	1000	1020	1020
Volume of PBS buffer	30	30	30	30	30	30	30	30
Operation Pressure	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Absorbance of Raw water	1.5540	1.5450	1.5150	1.4950	1.5060	1.4960	1.5070	1.507
Absorbance of Filtered water	1.3320	1.3620	0.9370	1.1750	0.9560	1.1940	1.2750	1.313
Concentration of Raw water	1100	1082	1030	1000	1018	1000	1020	1020
Concentration of Filtrate	735	782	80	471	110	485	640	700
R= (1-Cp/Cf)*100	33.1818182	27.7264325	92.2330097	52.9	89.194499	51.5	37.254902	31.372549
Average Rejection		30.4541254		72.5665049		70.3472495		34.3137255

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