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Synthesis and Characterization of Polyvinyl Alcohol Based Membrane

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Abstract: Poly-vinyl alcohol (PVA) is a polymer that has been a popular choice for membrane fabrication due to its excellent film-forming characteristics, outstanding chemical and mechanical stability, and tunable hydrophilicity. This research aims to develop hydrophilic membrane using PVA, chitosan and starch as the major ingredients and optimize the formulation of membrane using Response Surface Methodology (RSM), hence characterize in terms of physical, chemical and mechanical properties. The characterization of membrane were carried out using Fourier-Transform Infrared (FTIR) Spectroscopy to identify functional groups and chemical bonds involved, and also Scanning Electron Microscopy (SEM) to identify its morphology of the membrane. The optimizations of membrane using RSM were conducted with two responses which are swelling index and Water Vapour Transmission Rate (WVTR). The function of these responses are to identify the ability of the membrane to absorb water and the capability of water vapour to pass through the membrane. Based on the analysis, the membranes showed the optimized conditions at R^2 value obtained 91.64% for swelling index and 89.51% for WVTR, which proven that the membrane is hydrophilic and very selective to water.

Keywords: Poly-vinyl Alcohol, Chitosan & Starch, Membrane, Optimization

1. Introduction

Pervaporation membrane technology has received a lot of attention in recent decades and has proven to be a good alternative to traditional energy-intensive separation procedures like distillation columns [1]. The beauty of this technique resides in its low energy consumption, ease of design, low cost, and environmental friendliness [2]. It has recently been employed with effectiveness in the water treatment especially in removing organic solvent from water.

Nowadays, there are vast variety of membrane technologies have been widely employed in industries such as pervaporation, ultrafiltration, gas separation, reverse osmosis, controlled drug delivery, and as an electrolyte and electrode material in polymeric electrolyte fuel [3].

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As the polluted river cases is getting worse, a solution should be taken such as using membrane technology [4]. Hence, the aim of this study is to develop hydrophilic membrane using Polyvinyl Alcohol (PVA), chitosan and starch as the major ingredients. Membrane formulation is optimized using Response Surface Methodology (RSM) and then characterize the PVA based membranes in terms of its functional groups, swelling index, and its morphology and water vapour transmission rate.

This study aims on the development of a hydrophilic densed PVA based membrane that can separate water from any other organic substances as well as the development of natural and biodegradable chitosan and starch based membranes, with the goal of ensuring that the membranes were relatively hydrophilic and were very selective to water, making them potentially useful for the separation of organic solvent-water mixtures [5].

2. Materials and Methods

2.1 Materials

Materials and the equipments used are PVA, sago starch, chitosan, acetic acid, glycerol, beakers, hot plate, magnetic stirrer, glass petri dish, analytical balance, water heater, and drying oven and tea bag filters. All materials are available in the Lab of Biology and Function 1 (MBF1), Universiti Tun Hussein Onn Malaysia and used without further purification.

2.2 Methods

2.2.1 Membrane Preparation

PVA, starch and chitosan were weighed by ratio of 1:1:1 and were mixed together according to RSM formulation. Chitosan solution was stirred with diluted acetic acid. Starch solution was prepared by adding with glycerol and was stirred at 90^{o}C. Meanwhile PVA solution was prepared by adding distilled water and the mixture was stirred at a 100^{o}C. After all three solutions was cooled down, it is mixed in a beaker for 45 minutes and casted on glass petri dish. Within 24 hours, the membrane was divided into three identical weight was peeled off and were placed into three glass petri dishes before being stored in a dessicator.

2.2.2 Membrane Formulation and Membrane Characterization

A set of formulation was generated and membrane formulation produced according to the RSM. The first response is swelling index and the second response is Water Vapour Transmission Rate (WVTR). Membrane chemical characterization was carried out using Fourier Transform Infrared Spectroscopy (FTIR) to identify its functional group. The physical characteristics was analysed using Swelling Index. About 13 membrane samples has been cut into size of 25 mm × 20 mm and immersed in distilled water for 24 hours at room temperature. Three membrane samples were used and the membrane was cut into small pieces and underwent gold coating before analysed uning Scanning Electron Microscope (SEM) in order to identify its morphological structure. WVTR of the 13 membranes samples were placed at the mouth of containers filled with water.

2.3 Equations

The equation involved in determining the swelling index percentage (%SI) is as follows:

$$\%SI = \frac{Wwet - Wdry}{Wdry} \times 100 \qquad \textbf{Eq. 1}$$

where w_{wet} is the final weight of a membrane after immersion whereas w_{dry} is the initial weight of a membrane before immersion.

The equation involved in assessing theWVTR is as follows:

$$WVTR = \frac{Weight\ of\ H2O\ lost}{time \times area} \qquad \textbf{Eq. 2}$$

where time is the total duration for 8 consecutive periods whereas area is the membrane area involved during the transmission.

3. Results and Discussion

3.1 Results

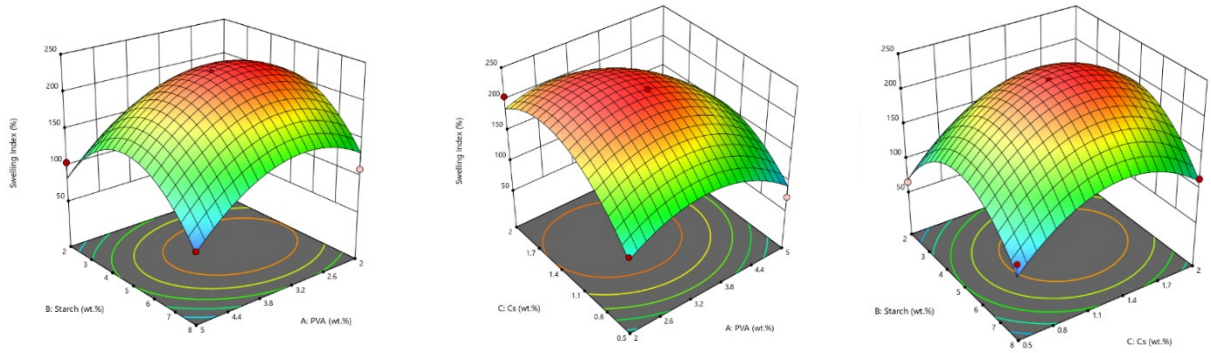
A sets of 13 membrane formulations have been produced according to Response Surface Methodology using Design Expert 7.0 software. Each formulation contributes to different amount of PVA, chitosan and starch.

3.1.1 Response Surface Methodolgy

According to **Figure 1(a)**, the value of PVA and St interact to determine the swelling index. Low concentration between PVA and St. produced the maximum SI value. The interaction that results might be explained by the existence of a relationship between the functional groups of PVA and starch, R2C(OR')2 and -OH [6][7]. Due to the potent hydrogen bonding interactions between the hydroxyl groups, starch and PVA demonstrated great compatibility.

Based on **Figure 1(b),** it shows the value of PVA and Cs interact to SI. The interaction between the concentration of PVA and Cs shows that SI decreases gradually along with the concentration of PVA while the concentration of Cs is increasing [8]. The resulting high SI was caused by the low concetration of PVA where the PVA consists of hydroxyl groups. The hydroxyl group which consists of PVA might develop a solid band of intermolecular and intramolecular [9][10].

According to **Figure 1(c)**, the value of St and Cs interact to produce the SI. Low concentration between St and Cs produced the greatest value of the SI. The variances were caused by the various even starch compositions of the two substances as well as the variable levels of chitosan and starch interaction [11]. The intensity of non-thermal mixing was lower than that produced by extensive thermal mixing though there was interaction between the two primary components.



(a) (b) (c)

Figure 1: 3D response surface plots for swelling index with different interactions of materials; (a) PVA-St interaction, (b) PVA-Cs interaction, (c) St-Cs interaction

Based on **Figure 2(a),** the value of PVA and St interact to WVTR. The highest value of WVTR is according to low concentration of PVA and St. This is because of a lower number of hydroxyl groups made them relatively hydrophilic with reasonable water resistance[12].

Based on **Figure 2(b)**, the reading of how PVA and Cs interact with WVTR is shown. At a high PVA concentration and low Cs concentration, the maximum value was attained. The interaction that results might be explained by the relationship between the functional groups of PVA and chitosan, -OH and -NH groups [13]. As a result of the functional group of PVA and Cs forming an intramolecular hydrogen bond. As a result, high permeability has been demonstrated using PVA and Cs.

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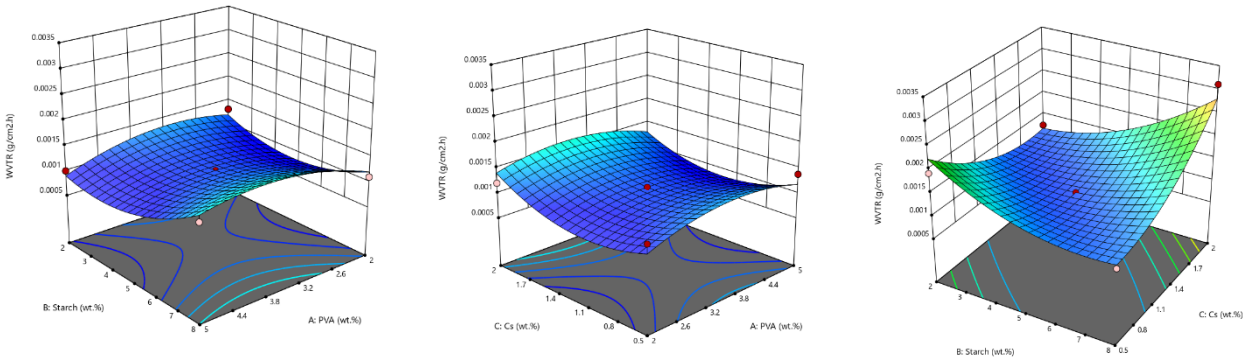
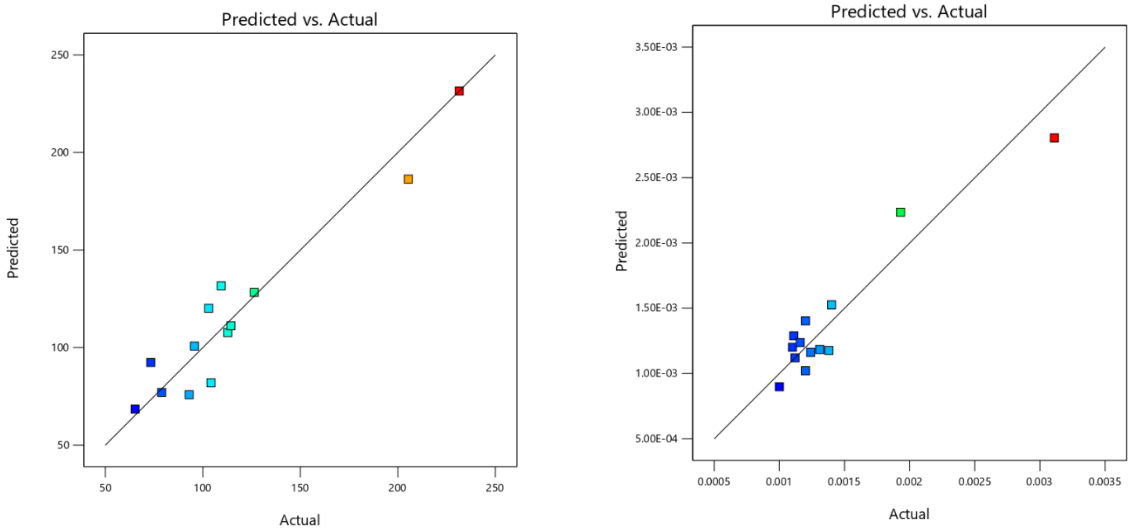


(a) (b) (c)

Figure 2: 3D response surface plots for Water Vapor Transmission Rate (WVTR) with different interactions of materials; (a) PVA-St interaction, (b) PVA-Cs interaction, (c) St-Cs interaction

The quadratic model from the Box-Behnken design was used to evaluate the polynomials responses model on these 13 data sets. As a result, the fitted model of the responses was estimated by comparing the predicted value plots to the actual values of the dependent variables, where the projected values were generated from the mathematical model and the actual values through experimental estimates[10]. By graphing the anticipated and actual values, Figure 3 illustrates the regression analysis. The statistical technique that calculated the link between the variables produced the regression data. Plotting of projected vs real values for the SI and WVTR is shown in **Figures 3(a)** and **Figure 3(b)**, where the gradient value appears to be close to the fitted diagonal line. The R^2 value for first response which is the swelling index is 0.9164 (91.64%) meanwhile R^2 value for second response which is the water vapour transmission rate (WVTR) is 0.8951 (89.51%). Thus, the R^2 obtained shows the model or membrane have high efficiency in separating organic solvent from water because the membrane shows its properties of high selectivity to water and hydrophilic and also the R^2 value are exceeds 85% indicate the minimum acceptable of good efficiency.



(a) (b)

Figure 3: Predicted against actual responses plot (a) SI and (b) WVTR

3.1.2 Fourier-Transform Infrared (FT-IR) Analysis

The spectra from the analysis collected the functional groups for the triplicate samples using Fourier-Transform Infrared. The first peak was appear at wavenumber value of 3728 cm^{-1}, 3262 cm^{-1}, 3275 cm^{-1} for membrane formulation 3, 2, and 1 respectively. These indicate that it has O-H stretching and have broad and strong absorption. After that, the medium peak at wavenumber value 2929 cm^{-1}, 2931 cm^{-1}, 2929cm^{-1} for membrane 3, 2, and 1 respectively and it was observed that it has vibration of hydrogen bonded C-H group. The spectrum of a strong at 1647 cm^{-1} is a clue of the C=C stretching that called alkene is present. Finally, the medium and sharp spectrum at wavenumber of 1077 cm^{-1} indicates that membranes have the primary alcohol. The example of spectra produced was shown in **Figure 4**.

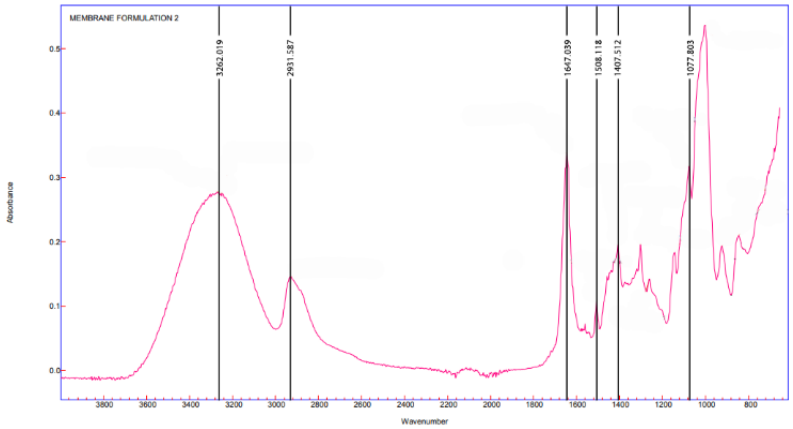


Figure 4: Fourier-Transform Infrared spectra result of a Membrane Formulation

3.1.3 Morphological Structure of Membrane

Based on **Figure 5**, SEM was used to examine the surface morphology of starch, PVA, and chitosan. The membrane's surface morphology for both PVA and pure starch was compact. Additionally, pure PVA and starch-based membranes exhibited smooth, flat surfaces, which suggested that exceptionally transparent, clear membranes were formed. Due to a particular phase separation, particle domains with sizes in the micron range were seen in certain membranes. The starch polymer reverted to the dispersed phase, which denotes in organic material from the liquid and represents the miscibility of the amorphous component of starch with PVA, as the PVA level increased. Strong bonding interactions were present, as seen by the hazy interface between two polymers [13].

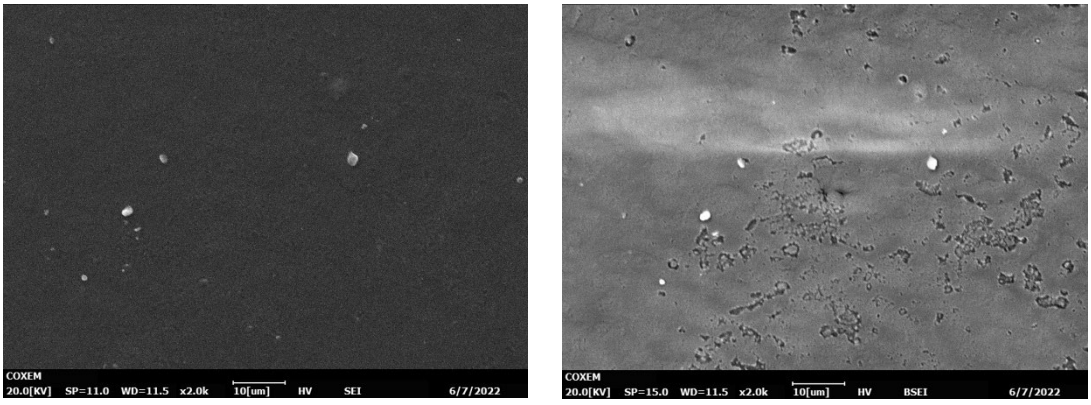


Figure 5: Scanning Electron Microscopy (SEM) of a Membrane formulation

4. Conclusion

Therefore, membrane separation process is one of the best ways to separate water from organic compounds. Other than that, the membrane-based separation technologies have drawn utmost attention due to high selectivity, low energy consumption, moderate cost-to-performance ratio, and compact modular design. In this study, PVA, chitosan, and starch were used to evaluate the membranes in various

concentrations to separate the water and organic solvents. Using RSM, the presence of starch and glycerol content into the membrane formulations have shown that it enhances the performance of separation between water and organic solvent in terms of SI and WVTR. The membrane also shows in good optimization which is the R^2 value for WVTR is 0.8951 and R^2 value for SI is 0.9164. FTIR analysis on the other hand shows that the membrane have functional groups of alcohol and alkene but mainly strong to alcohol because of PVA. The SEM shows a magnification of 2000× towards the surface of the membranes to identify its morphology and showing the excellent compatibility of starch with PVA-Cs helps to improve the mechanical behavior or its elasticity, and the smoother surface was observed. Thus, membrane technology should be widely explored as it has much benefits in terms of its properties as an advanced filtration system in the future.

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