# การเตรียมและการศึกษาคุณลักษณะของเยื่อเลือกผ่านแบบเมทริกซ์ผสมของยางธรรมชาติผสมพอลิไวนิลแอลกอฮอล์และซีโอไลท์

# Mixed matrix membranes of natural rubber-poly (vinyl alcohol) blend filled with zeolite: preparation and characterization

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## บทคัดย่อ

เยื่อเลือกผ่านแบบเมทริกซ์ผสมของยางธรรมชาติผสมพอลิไวนิลแอลกอฮอล์และซีโอไลท์ชนิด 4A ถูกเตรียมขึ้น พอลิไวนิลแอลกอฮอล์ถูกทำการเชื่อมขวางด้วยกรดซัลโฟซักซินิกในยางธรรมชาติซึ่งโครงสร้างที่ได้เป็นแบบ semi-IPN ศึกษาการเกิดการเชื่อมขวางของพอลิไวนิลแอลกอฮอล์ในเยื่อเลือกผ่านโดยใช้เทคนิคอินฟาเรดสเปกตรัม ผลการศึกษาการบวมตัวของเยื่อเลือกผ่านทั้งในน้ำและเอทานอลพบว่าค่าการบวมตัวของเยื่อเลือกผ่านเพิ่มขึ้นตามปริมาณของพอลิไวนิลแอลกอฮอล์ในเยื่อเลือกผ่านที่เพิ่มขึ้น อย่างไรก็ตามผลในการบวมตัวของเยื่อเลือกผ่านลดลง เมื่อทำการเติมซีโอไลท์ที่ปริมาณมากกว่า 10%โดยน้ำหนัก จากการศึกษาสภาวะของน้ำในเยื่อเลือกผ่านด้วยเทคนิค DSC พบว่าปริมาณของ bound water เพิ่มขึ้นตามปริมาณของพอลิไวนิลแอลกอฮอล์ในเยื่อเลือกผ่านที่เพิ่มขึ้นแต่ลดลงตามปริมาณของซีโอไลท์ที่เพิ่มขึ้น การศึกษาสลายตัวทางความร้อนของเยื่อเลือกผ่านด้วยเทคนิค TG-DTA พบว่าเยื่อเลือกผ่านแบบผสมเสถียรต่อความร้อนมากกว่ายางธรรมชาติและพอลิไวนิลแอลกอฮอล์เนื่องมาจากการเติม ซีโอไลท์ การศึกษาการกระจายตัวของอนุภาคซีโอไลท์ในเยื่อเลือกผ่านด้วยเทคนิค SEM พบว่าอนุภาคซีโอไลท์เกิดการกระจายตัวได้ดีในเยื่อเลือกผ่าน

## Abstract

Mixed matrix (MM) membranes of natural rubber (NR) - poly(vinyl alcohol) (PVA) blend filled with zeolite 4A were prepared. PVA was crosslinked with sulfosuccinic acid (SSA) in the immediate presence of NR to form a semi-interpenetrating polymer network structure. The crosslink of PVA in the MM membrane was confirmed by FT-IR spectroscopy. The swelling behaviours of the membranes were investigated and the degree of swelling in water and ethanol was found to increase with increasing PVA content in the membranes however adding the zeolite more than 10 wt.% leaded to the decreasing of membrane swelling. The states of water in the membranes were studied using differential scanning calorimeter (DSC). The amount of bound

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water in the membranes increased with increasing PVA but decreased with the amount of zeolite. The thermal degradation of the MM membrane was determined using TG-DTA analysis. The MM membranes showed a higher thermal stability compared with pure NR and PVA due to the incorporation of zeolite. The SEM micrographs of MM membranes showed a well dispersing of zeolite particles in the NR-PVA blend matrix.

**คำสำคัญ:** พอลิไวนิลแอลกอฮอล์ ซีโอไลท์ เยื่อเลือกผ่าน เมทริกซ์แบบผสม

**Keywords**: Poly (vinyl alcohol), Zeolite, Membrane, Mixed-Matrix

## 1. Introduction

Pervaporation is an efficient membrane process for liquid mixtures separation. Pervaporation is a combined process of the permeation and evaporation. In pervaporation process, liquid mixtures are fed under pressure to a membrane and the separated component passes through the membrane by solution diffusion mechanism before evaporates at the permeate side of the membrane where vacuum is applied. Typically pervaporation membranes can be classified as the hydrophobic and hydrophilic type. Hydrophilic membranes have the affinity for water or other polar compounds. Hydrophilic membranes include both ionic and non-ionic membranes. The non-ionic membranes generally contain polar chemical groups such as hydroxyl, carboxyl, sulfonyl, carbonyl, or amine groups. Examples of hydrophilic non-ionic membranes include poly(vinyl alcohol) (PVA), cellulose acetates, and poly (vinyl amine). Hydrophobic membranes, on the other hand, have little affinity for water or polar compounds and generally lack or contain a small proportion of charged or polar chemical groups. Examples of hydrophobic membranes include polyethylene and polystyrene. Hydrophilic membranes can be used for the separation of azeotropic solvent mixtures containing water (E. Ruckentein and L. Liang, 1996). Hydrophobic membranes used for the preferential permeation of organic solvents from organic/ water solutions or organic/ organic mixtures (Wojciech C. et al, 2004). In this study, dense membranes were prepared from blend of hydrophilic PVA and hydrophobic NR. PVA is hydrophilic polymer with a good film formation. However it is highly swollen in water that cause a reduction in water separation efficiency. By blending these two polymers, the swelling of the membrane can be controlled and the water separation is more efficient. In addition, mixed matrix membranes were prepare by incorporating zeolite 4A which a pore size of 4 $^{o}$A into dense membrane. Because of the porous structure of zeolite, flux across the membrane can be enhanced while the separation efficiency can be maintained.

## 2. Experimental method

### 2.1. Materials

Poly (vinyl alcohol) with Mw = 186,000 g/mol and 89%hydrolyed was purchased from Aldrich. Concentrated natural rubber latex (60%DRC) was obtained from Thai Hua Rubber, Thailand. Sulfosuccinic acid was purchased from Aldrich. Zeolite (4A) was provided by PQ Chemical, Thailand. Triton X-405 for stabilization of NR was obtained from Sigma-Aldrich.

### 2.2. Membranes preparation

NR/PVA membranes were prepare by dissolving PVA in deionized water, subsequently the NR latex and triton X-405 were added to the PVA solution. SSA was added to crosslink PVA in the immediate present of NR using 1 mol per 8 mol of VA unit. Then the dispersions was constantly stirred at 70 °C for 3 hours. The resultant dispersion was cast on a glass plate and the cast membrane was dried at 40 °C for 48 hours. The compositions of NR/PVA membranes are shown in Table 1. The preparation of the mixed matrix membranes is similar to the preparation of the NR/PVA membranes except that zeolite was added into the PVA solution before adding NR latex. The compositions of the mixed matrix membranes are shown in Table 2.

### 2.3. Membranes characterisation

*2.3.1. Fourier transform infrared (FT-IR) spectroscopy*

The FT-IR spectra of the membranes were obtained by using PerkinElmer, spectrum one FT-IR spectrometer measuring at wavenumber of 4000 -400 $cm^{-1}$.

*2.3.2. Thermal gravitometry (TG) analysis*

Thermal stability of the membranes was examined using PerkinElmer pyris diamond TG/DTA from 30 to 600 C with heating rate of 10 °C/min under nitrogen.

*2.3.3. Differential scanning calorimeter (DSC)*

PerkinElmer Pyris 1 DSC was used for studying the free water and bound water of the membranes. The sample was cooled down to -50 before heated to 50 °C with heating rate of 5 °C/min in the nitrogen atmosphere.

*2.3.4. Scanning electron microscopy (SEM)*

The cross-sectional and the surface of the membranes were observed using Scanning electron microscopy (SEM) (LEO 1450 VP). All specimens were coated with a conductive layer of sputtered gold.

*2.3.5. Swelling measurements*

The swelling of the membranes was determined gravimetrically. The degree of swelling in the membranes was measured by immersing the dry membrane Wd in the deionized water for 48 hours. Then the membrane was taken out, wiped with filter paper, and immediately weighed Ww. The degree of swelling (%DS) was calculated as:

$$DS(\%) = \frac{Ws - Wd}{Wd} \times 100 \qquad (1)$$

**Table 1** Compositions of the NR/PVA membranes

| Membrane | NR /PVA (wt. %) | NR (g) | PVA (g) | SSA (g) |
|---|---|---|---|---|
| NR/PVA-10 | 90/10 | 15 | 1.67 | 0.67 |
| NR/PVA-20 | 80/20 | 15 | 3.75 | 1.51 |
| NR/PVA-30 | 70/30 | 15 | 6.43 | 2.58 |
| NR/PVA-40 | 60/40 | 15 | 10.0 | 4.02 |

**Table 2** Compositions of the mixed matrix membranes

| Membrane | (PVA+NR) /Zeolite (wt.%) | NR (g) | PVA (g) | SSA (g) | Zeolite (g) |
|---|---|---|---|---|---|
| NR/PVA-Zeo10 | 90/10 | 15 | 1.67 | 0.67 | 1.85 |
| NR/PVA-Zeo20 | 80/20 | 15 | 1.67 | 0.67 | 4.17 |
| NR/PVA-Zeo30 | 70/30 | 15 | 1.67 | 0.67 | 7.14 |
| NR/PVA-Zeo40 | 60/40 | 15 | 1.67 | 0.67 | 11.11 |

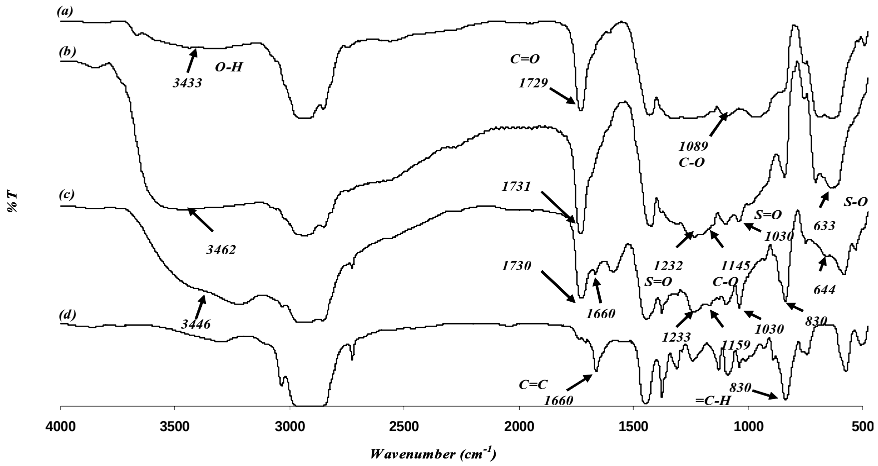

**Figure 1.** FTIR spectra of (a) un-crosslink PVA, (b) crosslink PVA, (c) NR/PVA-40 and (d) NR.

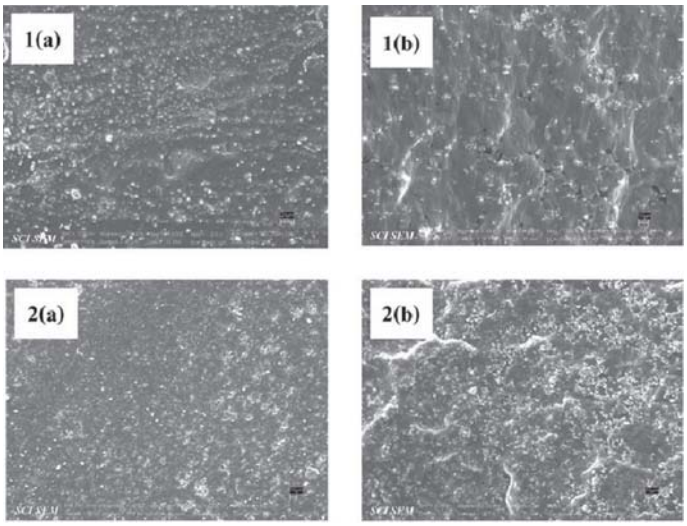

**Figure 2.** SEM micrographs of membranes: (1) NR/PVA-Zeo10, (2) NR/PVA-Zeo40, (a) surface and loss of water (b) cross-section.

## 3. Results and discussion

### 3.1. FT-IR spectra

The FT-IR spectra of un-crosslink PVA, crosslink PVA, NR/PVA-40 (40 wt.% PVA content) and NR were shown in Figure 1. The un-crosslink PVA spectrum showed a broad absorption band around 3400 $cm^{-1}$ corresponding to O-H stretching. The peak at 1729 $cm^{-1}$ corresponds to the acetate group on PVA main chain (Shubhangi G et al., 2004). For crosslink PVA, the C=O group linkage was observed at 1731 $cm^{-1}$. The characteristic peaks of NR can be observed at 830 and 1660 $cm^{-1}$ corresponding to the stretching and bending of the C=C of isoprene unit. For NR/PVA membrane all characteristic peaks of both crosslinked PVA and NR were observed, indicating that PVA was crosslinked in the presence of NR forming a semi-IPN structure.

### 3.2. SEM

Figure 2 shows the SEM micrographs of cross-section and surface of the mixed matrix membranes. The zeolites were well dispersed within the polymer matrix. However some of zeolite aggregates can be observed for 40% zeolite loading.

### 3.3. TG studies

Figure 3 and Figure 4 shows the TG curves of the NR/PVA membranes and the mixed matrix membranes, respectively. The weight loss of NR/PVA membrane can be divided into 4 steps. The first weight loss at 100-170 °C was due to the loss of water and second weight loss at 170-240 °C corresponded to the crosslink breakage. The third weight loss at 240-380 °C was main chain NR decomposition and the last weight loss at 380-480 °C can be attributing to PVA degradation. For the mixed matrix membranes, there were the residual after 600 °C which was mainly zeolite.

### 3.4. Degree of swelling of the membranes

*The effect of PVA content.*

Figure 5 shows degree of swelling of NR/PVA membranes in water and ethanol. It can be seen that the degree of swelling both in water and ethanol increased with increasing PVA content. However the degree of swelling in water increased more significantly than those of swelling in ethanol due to the hydrophilicity of PVA.

*The effect of zeolite loading.*

Figure 6 shows the degree of swelling of MM membranes. It can be seen that the degree of swelling of MM membranes decreased upon increasing zeolite loading. However for zeolite filled NR/PVA membrane the trend are different in which the degree of swelling increased at low zeolite loading before started to decrease for high loading of zeolite. However adding high zeolite loading in NR/PVA membranes will result in a less amount of PVA affecting the hydrophilicity of membrane to decrease.

### 3.5. The states of water

In general, the states of water in a polymer can be divided into free water, freezing bound water and non- freezing bound water. Free water will appear as transition peak at 0 °C, which is the freezing point of bulk water. If water molecules have specific interactions with polymer, the transition peak will shift to lower temperature and this is called freezing bound water. Non- freezing bound water is the water which shows no detectable transition due to the strong interaction with the polymer (Samuel P et al., 2000). The DSC thermograms of both NR/PVA membrane and mixed matrix membrane showed only peak at 0 °C. The amount of free water can be estimated from the DSC peak area divided by the specific melting enthalpy of pure water (334000 J/g). Bound water is equal to total adsorbed water minus free water.

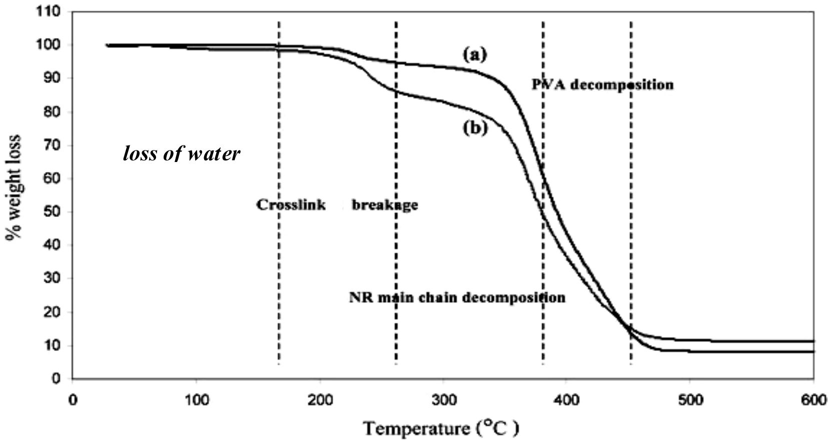

**Figure 3.** TG curves of the membranes: NR/PVA-10 (a) and NR/PVA-30 (b).

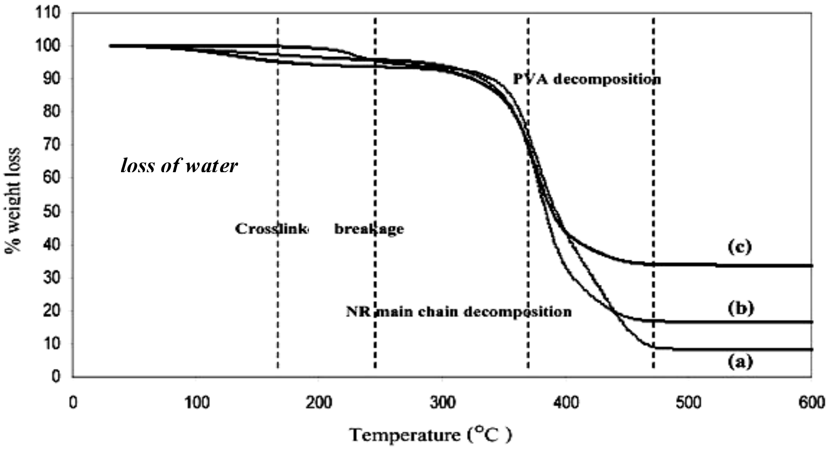

**Figure 4.** TG curves of the membranes: (a) NR/PVA-10, (b) NR/PVA-Zeo20 and (c) NR/PVA-Zeo40.

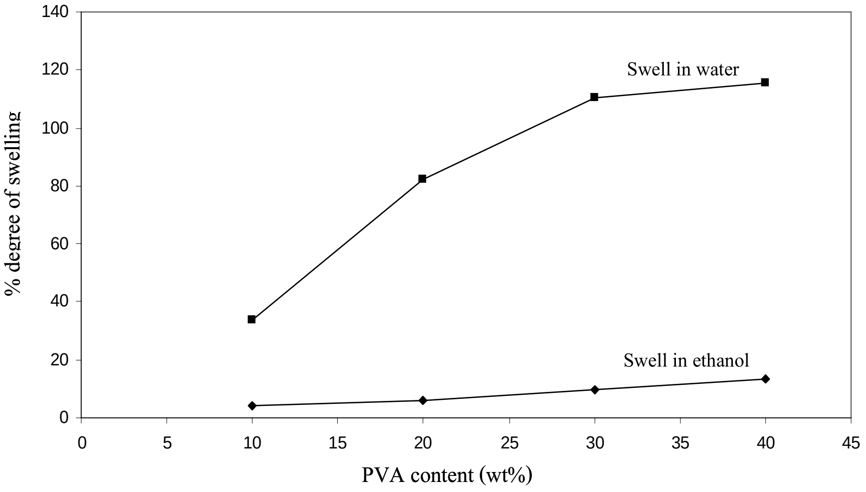

**Figure 5.** Degree of swelling of NR/PVA membranes in water and ethanol.

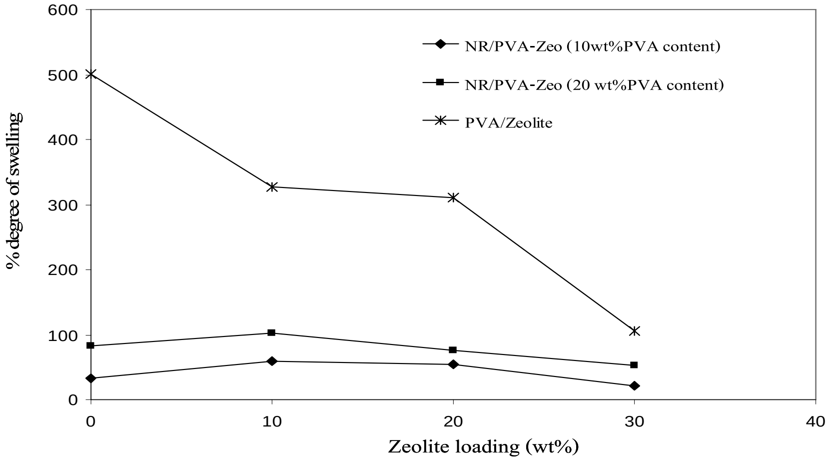

**Figure 6.** Degree of swelling of MM membranes in water.

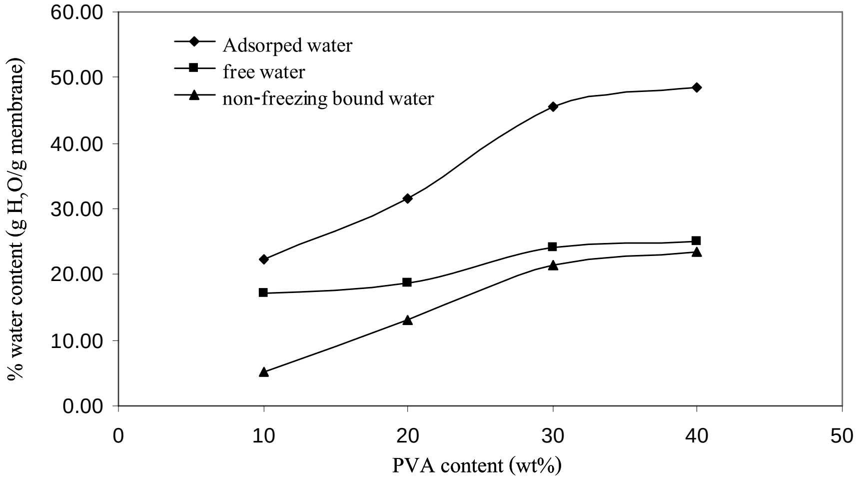

**Figure 7.** The states of water uptake in the NR/PVA membranes.

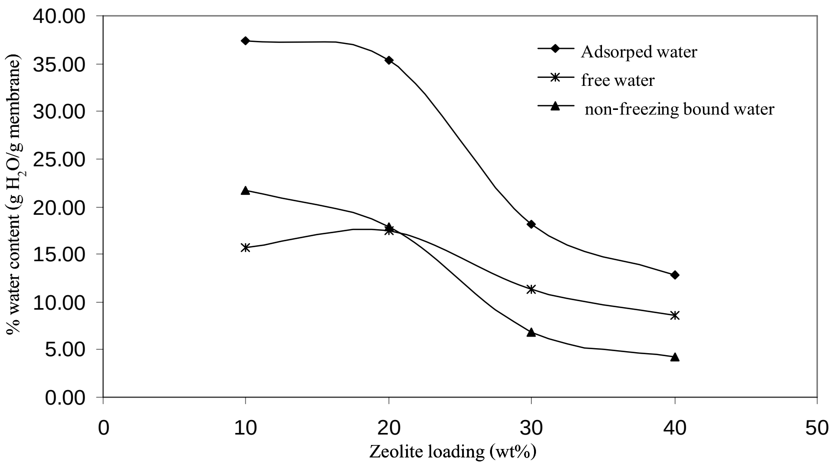

**Figure 8.** The states of water uptake in the mixed matrix membranes.

Figure 7 shows the states of water in the NR/PVA membranes. The results showed that both free water and non-freezing bound water increased with increasing PVA content indicating that water molecules have more interaction with the membrane due to the increasing of hydroxyl functional groups. Figure 8 shows the states of water in the mixed matrix membranes. The results showed that both free water and non-freezing bound water decreased with increasing zeolite loading. Since the water sorption capability of zeolite is less than that of PVA, therefore increasing zeolite loading will result in a less amount of PVA affecting the total water sorption capacity of the mixed matrix membrane to decrease.

## 4. Conclusion

The mixed matrix membranes were successfully prepared from natural rubber blend with crosslink-poly (vinyl alcohol) and filled with zeolite. The degree of swelling in water was found to increase with increasing PVA content in the membranes however adding the zeolite more than 10 wt.% leaded to the decrease of membrane swelling. The mixed matrix membranes showed higher thermal stability than NR and NR/PVA membrane. The states of water from DSC indicated that there were free water and non-freezing bound water with in NR/PVA membrane and increasing PVA content resulted in increasing of both free water and non-freezing bound water. However for mixed matrix membrane increasing zeolite loading resulted in decreasing of both free water and non-freezing bound water.

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