

Effects of MgO Particle Loading on Gas Permeation Properties of Epoxidized Natural Rubber (ENR) / Polyvinyl Chloride (PVC) Membrane

(Kesan Penambahan Partikel MgO ke atas Ketelapan Gas bagi Membran Getah Asli Terepoksida (ENR) / Polivinil Klorida (PVC))

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ABSTRACT

A composite membrane was prepared by mixing epoxidized natural rubber (ENR) and polyvinyl chloride (PVC). An inorganic filler, MgO, was introduced into the polymer matrix by certain percentages to form a mixed matrix membrane (MMM). The resulting membranes were characterized using FTIR, TGA, SEM and gas permeability test. FTIR results showed the incorporation of MgO inside the membrane matrix with the appearance of an absorption peak at 3700 cm^{-1} which represents the formation of $\text{Mg}(\text{OH})_2$. Thermogram from TGA analysis showed two degradation stages at $250\text{--}350^\circ\text{C}$ and $370\text{--}500^\circ\text{C}$, which correspond to the decomposition of PVC and ENR and the residue of fillers at 600°C . SEM images of the membranes showed that pores were developed as fillers were introduced to the membrane. The size of the pores also increased with the increase of filler percentage. As for gas permeation test, the permeability values of CO_2 and N_2 for ENR/PVC membrane were the lowest. The permeability values increased with the addition of MgO to the membrane. The permeability of CO_2 was also the highest for all membranes.

Keywords: ENR-50; gas separation; inorganic filler; polyvinyl chloride

ABSTRAK

Membran komposit telah disediakan dengan mencampurkan getah asli terepoksida (ENR) dengan polivinil klorida (PVC). Pengisi tak organik (MgO) telah dimasukkan ke dalam matriks polimer tersebut dengan peratusan tertentu untuk menghasilkan membran campuran matriks (MMM). Membran yang terhasil telah dicirikan dengan menggunakan FTIR, TGA, SEM dan ujian ketelapan gas. Keputusan ujian FTIR telah menunjukkan kehadiran MgO di dalam matriks membran apabila terdapat puncak serapan pada 3700 cm^{-1} yang mewakili pembentukan $\text{Mg}(\text{OH})_2$. Termogram daripada analisis TGA menunjukkan dua peringkat penguraian, iaitu pada $250\text{--}350^\circ\text{C}$ dan $370\text{--}500^\circ\text{C}$ yang mewakili penguraian PVC dan ENR. Residu pada suhu 600°C pula adalah disebabkan pengisi yang tidak terurai. Mikrograf daripada ujian SEM menunjukkan kehadiran liang dengan kehadiran pengisi di dalam matriks membran. Saiz liang juga dilihat bertambah dengan penambahan peratusan pengisi. Untuk ujian ketelapan gas, nilai ketelapan gas CO_2 dan N_2 bagi membran ENR/PVC adalah yang terendah. Nilai ketelapan dilihat semakin meningkat dengan penambahan MgO ke dalam membran. Ketelapan gas CO_2 pula adalah yang tertinggi bagi semua membran.

Kata kunci: ENR-50; pemisahan gas; pengisi tak organik; polivinil klorida

INTRODUCTION

Recently, a wide range of polymeric membranes were studied aggressively in search of gas separation process with low price, economical processability, good thermostability and high energy efficiency (Chung et al. 2007; Ge et al. 2011). The studied polymers include polyisoprene and thermoplastic polymers such as polycarbonate, polystyrene and polyvinylchloride (Chen et al. 2000; Dobre et al. 2011; Nagasaki et al. 1996; Rajabi et al. 2013). Johnson and Thomas (1999) stated that the membrane for gas separation process needs to meet several criteria which are high permeability to the desired gas, high selectivity and resistance to processing conditions. However, the drawback in gas separation membrane research is the trade-off limitation between gas permeability and selectivity (Robeson 2008, 1991).

To overcome this problem, mixed matrix membrane (MMM), the mixture of organic polymer matrix with inorganic particles as fillers, is believed to be the alternative in optimizing permeability and selectivity of polymeric membranes. The addition of fillers also increases thermal stability, physical properties and mechanical strength of the membrane (Chung et al. 2007). Inorganic fillers also act to create preferential permeation pathways for selective permeability while posing a barrier for undesired permeation in order to improve separation performance (Jadav & Singh 2009). Moreover, the fillers can solve the fragility inherent usually found in polymeric membranes (Goh et al. 2011). The filler used must be compatible with the membrane matrix in order to prepare a homogenous and stable MMM. Some of the inorganic particles used as fillers in MMM include silica,

zeolites and metal oxides (Şen et al. 2007; Wahab et al. 2012; Zulfikar et al. 2007).

In this study, epoxidized natural rubber (ENR) was blended with polyvinyl chloride (PVC) to produce an elastic and strong membrane. A study by Ibrahim and Dahlan (1998) reported that PVC has good interaction with ENR. PVC is expected to provide mechanical strength to the membrane, while ENR assists the permeability and selectivity. However, ENR should be used in higher proportion in order to produce a blend that is flexible and mechanically tough to be used as a self-supporting membrane (Jon et al. 2013).

Inorganic filler used in this study is magnesium oxide (MgO). The filler was introduced inside the polymer matrix by certain percentages by mass before the membrane was produced. The incorporation of MgO inside the membrane was expected to improve the gas permeability of the membrane as the percentage increased. The effect of filler addition to chemical, physical and gas permeation properties were discussed at the end of this study.

EXPERIMENTAL DETAILS

MATERIALS

ENR-50 used in this study was supplied by Malaysian Rubber Board. The PVC was supplied by Industrial Resin (M) Ltd., tetrahydrofuran (THF) by System and MgO by Merck.

ENR/PVC AND ENR/PVC/MGO MEMBRANE PREPARATION

The preparation of ENR/PVC thermoplastic elastomer (TPE) was done by blending the PVC with epoxidized natural rubber (ENR-50) using a melt blend internal mixer at the temperature of 160°C for approximately 13 min. Several ratio of ENR to PVC have been studied but the best ratio for a cured composite and flexible self-supporting membrane was 60:40 (w/w %), which was then employed in this study. ENR/PVC matrix was dissolved in THF for 24 h with the ratio of 1:8 (w/v). Swollen polymer matrix was then stirred with magnetic stirrer for another 24 h until a homogeneous solution was obtained. In preparing the ENR/PVC membrane, the solution was casted using casting knife onto a flat glass plate. The preparation of ENR/PVC/MgO membrane was done by adding MgO to the ENR/PVC solution with 2, 5 and 8% (w/w %). These percentages were used to study the effects of different amount of MgO on the properties of the membranes. MgO was not added more than 8% because higher loading will result in high agglomeration and the membrane become brittle. Then, ENR/PVC/MgO solution was stirred for another 24 h before it was casted. The thickness of the membrane was set to be approximately 0.25 mm. The casted membrane was immersed in distilled water for solvent exchange to occur before being peeled off. The membrane prepared was then stored to dry before characterization.

CHARACTERIZATION

The membranes functional groups were determined using Perkin Elmer Fourier Transform Infrared Spectroscopy, (GX FTIR System). Thermal gravimetric analysis was carried out using a Mettler Toledo thermogravimetric analyser (TGA/SDTA 851), performed under nitrogen atmosphere over temperature range of 50-600°C with 20°C·min⁻¹ heating rate and scanning electron microscopy was used to observe the morphology of the membranes.

GAS PERMEATION TEST

Gas permeation properties of the membranes were tested using constant pressure/variable volume technique. The gases used were purified nitrogen (N₂) and purified carbon dioxide (CO₂). The pressures used for the permeability test were 2, 4, and 6 bars at room temperature. Gas permeability was determined using (1):

$$P = \frac{ql}{A(p_1 - p_2)}, \quad (1)$$

where P is the permeability expressed in Barrer (1 Barrer = 10⁻¹⁰ cm³ (STP) cm/cm²·s·cmHg), q is the flow rate of the permeated gas passing through the membrane (cm³/s), l is membrane thickness (cm), A is the effective membrane area (cm²), while p₁ and p₂ are the absolute pressure of the feed side and permeate side, respectively (cmHg).

The selectivity coefficient, α of the membrane was calculated from the permeability (P) obtained from (1) using (2),

$$\alpha = \frac{P_{CO_2}}{P_{N_2}}, \quad (2)$$

where P_{CO₂} is the permeability value of CO₂ and P_{N₂} is the permeability value of N₂ gas.

RESULTS AND DISCUSSION

FTIR ANALYSIS

Figure 1 shows the FTIR spectrum for ENR/PVC and ENR/PVC/MgO membranes. Both the spectrums show similar peaks of ENR and PVC functional groups, except for the peak at 3700 cm⁻¹ for ENR/PVC/MgO membrane, which is attributed to the presence of Mg(OH)₂ as reported by Foster et al. (2002). This was due to the interaction of MgO with moisture. Apart from that distinctive peak, similar absorption peaks for both membranes were observed in the range of 3000-2800 cm⁻¹, which corresponded to the C-H stretching. The peak at 1450 cm⁻¹ marks the presence of C-H bonding while the bands at 1254 cm⁻¹ corresponded to the C-O-C asymmetric vibration. The presence of C-O-C vibration of epoxy ring can be seen at the absorption peak of 874 cm⁻¹, while the absorption peak of C-Cl functional group of PVC is represented by the absorption peak 699 cm⁻¹ (Bandyopadhyay et al. 2006). The broad peaks at 3459 cm⁻¹

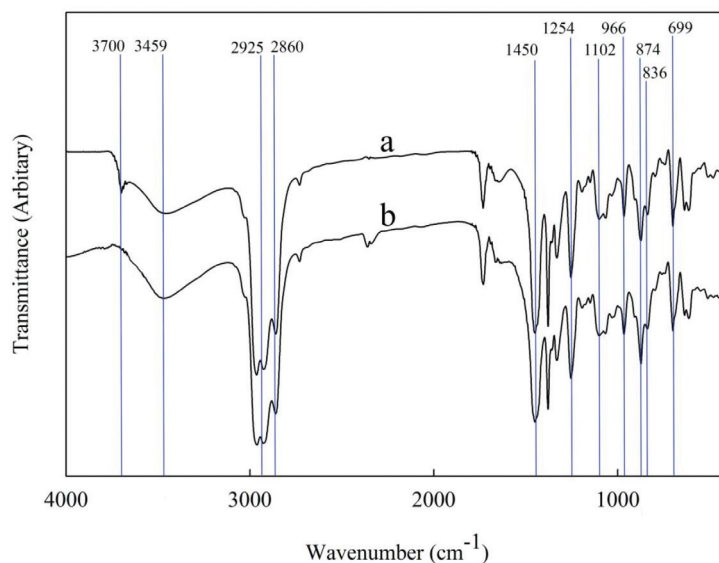


FIGURE 1. FTIR spectrum of a) ENR/PVC/MgO and b) ENR/PVC membrane

for both membranes are attributed to the presence of OH functional group that might result from the water used during the preparation of the membrane.

THERMOGRAVIMETRIC ANALYSIS (TGA)

Thermogravimetric analysis was done to study the decomposition of the membranes. Figure 2 shows the TGA curves of ENR/PVC and ENR/PVC/MgO membranes. Referring to the figure, two clear degradation stages can be seen. The first degradation stage of the membranes is at the temperature range of 250-350°C. Degradation at this temperature can be assigned to the degradation of PVC matrix (Blazevska-Gilev & Spasesk 2010). The second degradation stage occurs at the temperature range

of 370-500°C, which can be attributed to the degradation of polyisoprene chains in ENR (Hakim & Ismail 2009).

Membrane with no filler was observed to have the lowest residual percentage at 600°C, followed by membrane with 2, 5 and 8% MgO. Referring to Table 1, the residual percentage of ENR/PVC membrane is 4.9% compared with membranes with MgO fillers. This was due to the amount of fillers used in those membranes. MgO degrades at temperature higher than 600°C, explaining the residues left at that particular temperature. Table 1 also shows that the MgO residual percentages are less than the initial percentages used as fillers. This could be the result of fillers being leached out of the membranes during the phase inversion process.

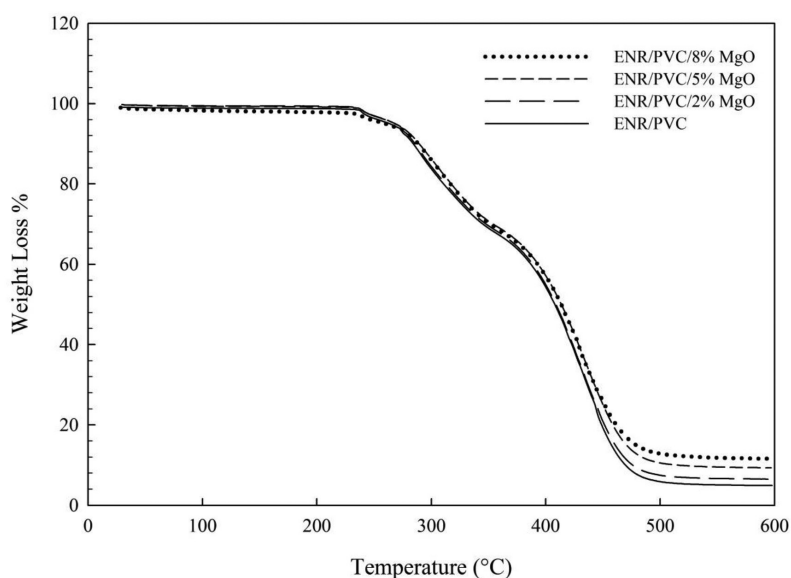


FIGURE 2. TGA curves for ENR/PVC membrane with 2, 5 and 8% MgO fillers

TABLE 1. Residual percentages of membranes and fillers

Membrane	Filler's initial amount (%)	Membrane residues (%)	Filler residues (%)
ENR/PVC	0	4.9	0
ENR/PVC/2% MgO	2	6.5	1.6
ENR/PVC/5% MgO	5	9.3	4.4
ENR/PVC/8% MgO	8	11.6	6.7

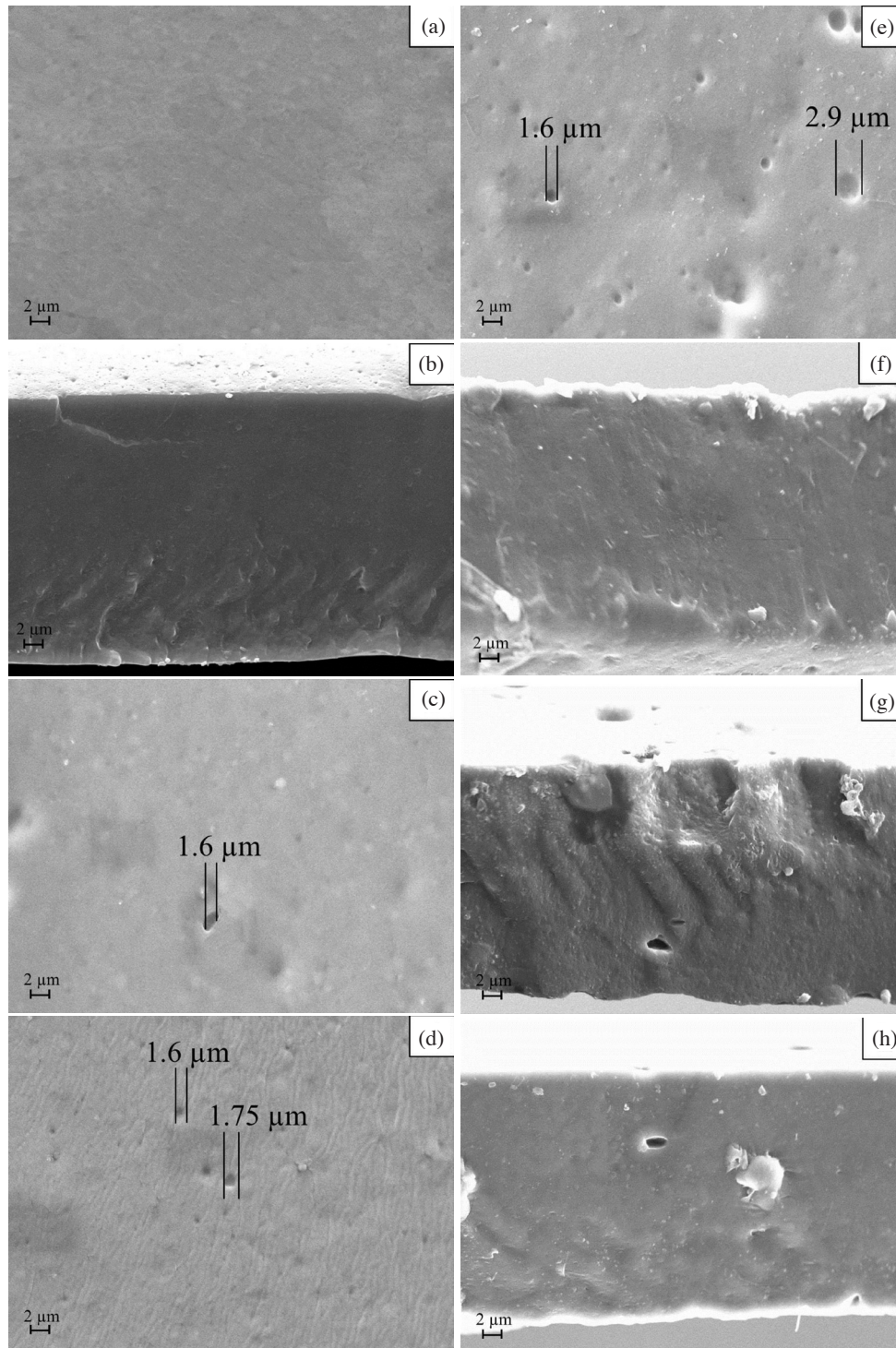


FIGURE 3. SEM images of a) ENR/PVC membrane surface, b) ENR/PVC membrane cross section, surfaces of c) ENR/PVC/2% MgO, d) ENR/PVC/5% MgO, e) ENR/PVC/8% MgO and the cross sections of f) ENR/PVC/2% MgO, g) ENR/PVC/5% MgO and h) ENR/PVC/8% MgO

MORPHOLOGY

Morphology of the membranes prepared were studied using scanning electron microscopy (SEM). SEM images at 5000 \times magnification of surfaces and cross sections of the membranes are shown in Figure 3. No pores can be seen on the surface and cross section of ENR/PVC membrane. However, as fillers were added to the membranes, pores were visible on the surfaces of the membranes. From Figure 3(c), 3(d) and 3(e), more pores seemed to be developed as more fillers were introduced into the membrane. Apart from that, increments of pore sizes were also observed. ENR/PVC/2% MgO membrane had pores with diameter ranging from 1.3-1.6 μm . Pore diameter of ENR/PVC/5% MgO membrane increased from 1.6-1.8 μm , while the pore diameter of ENR/PVC/8% MgO membrane increased from 1.4-2.9 μm . The cross sections of the filled membranes (Figure 3(f), 3(g), 3(h)) also show the integration of fillers inside the membrane matrix.

The presence of pores inside the membranes was due to the substitution of the dense structure of the polymer chains by the highly porous inorganic particles. This results in pores or microvoids to be developed (Hosseini et al. 2007). As more filler were present inside the membrane, more dense structures were being substituted, resulting in the formation of more microvoids. Pores might also develop as some of the fillers were leached out of the membrane during the phase inversion process, leaving voids inside the membrane matrix (Arthanareeswaran et al. 2008; Chen et al. 2010). Apart from that, the phase inversion itself can contribute to pore formation as the solvent exchange occurs between THF and water.

GAS PERMEATION PROPERTIES

Gas permeability test was carried out to study the effect of fillers addition to the membrane. The permeability of the

membranes is presented in Figure 4. The gas permeability values of ENR/PVC/MgO membranes are higher than the values of ENR/PVC membrane for both gases. The gas permeability increased with increasing amount of MgO added to the membrane. Carbon dioxide also exhibits higher permeability value compared to nitrogen gas for all membranes.

Several factors have been considered to have influenced the permeability results of these membranes. The first one is the presence of pores or microvoids inside the MgO filled membrane, resulting in higher permeability for both gases. However, since CO_2 has smaller kinetic diameter (3.3 \AA) than N_2 (3.64 \AA) (Khudyakov et al. 2009), CO_2 diffuses faster, resulting in higher permeability values for all membranes.

The permeability of the gases also influenced the selectivity coefficient of the membranes, as presented in Table 2. The difference in the permeability of CO_2 and N_2 (calculated using (2)) for ENR/PVC membrane can be observed due of the high selectivity values. Unfilled membrane is non-porous and dense, making the permeation of gases through it to depend on solution-diffusion mechanism. Thus, carbon dioxide permeates easier. However, in MgO filled membranes, pores were developed, resulting in high permeability and thus, low selectivity. This is consistent with the report by Scholes et al. (2008), stating that membrane with high permeability has low selectivity.

Another factor to be considered to have influenced the selectivity of the membranes is the interaction of gases with membrane matrix and filler surfaces. Matteucci et al. (2008) reported that there is interaction between CO_2 and MgO. This was due to the acidity of CO_2 , which results in high affinity of physisorption towards basic MgO and $\text{Mg}(\text{OH})_2$. The interaction results in large adsorption of

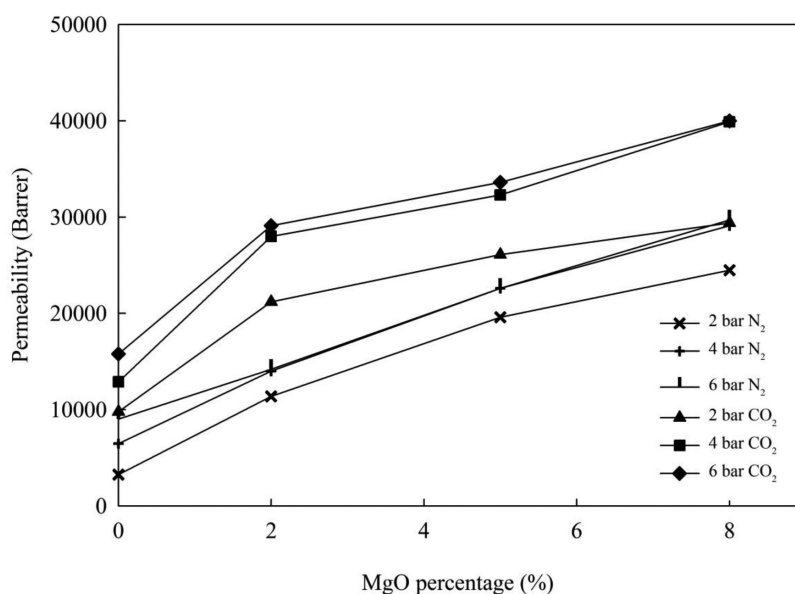


FIGURE 4. Gas permeability test result of ENR/PVC membrane and ENR/PVC/MgO membranes

TABLE 2. Selectivity (α) of CO₂/N₂ for ENR/PVC membrane and ENR/PVC/MgO membranes

Pressure (Bar)	ENR/PVC	ENR/PVC/2% MgO	ENR/PVC/5% MgO	ENR/PVC/8% MgO
2	3.0	1.8	1.3	1.2
4	2.0	2.0	1.4	1.4
6	1.7	2.1	1.5	1.4

CO₂ even at low pressure, which consequently enhanced the gas permeability and increased its selectivity. Nitrogen, however, is an inert gas, making permeability to depend only on its kinetic size which correlates with pore size of the membrane.

CONCLUSION

The addition of MgO into the ENR/PVC matrix has improved pore formation inside the membrane. Membrane with higher filler percentage was observed to exhibit more pores compared to membranes with lower filler percentage. Thermal degradation showed that some filler were leached out of the membrane during preparation. Higher filler loading also influenced gas permeability of the membranes. Membrane with 8% MgO was more permeable to both CO₂ and N₂ gases, with CO₂ permeation value being the highest for all membranes due to smaller kinetic diameter and interaction of the gas with fillers.

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