

## Influence of Silica Addition on the Properties of Epoxidised Natural Rubber/Polyvinyl Chloride Composite Membrane

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**ABSTRACT:** Flexible and porous epoxidised natural rubber (ENR)/polyvinyl chloride (PVC) membranes were prepared via phase inversion technique. The pore formation on ENR/PVC membranes was initiated with the introduction of inorganic particles (silica). Two types of silica, microsilica (microcrystalline silica powder) and nanosilica [generated from Tetraethoxysilane (TEOS)] were used. Effects of silica addition on the membrane structure are investigated by means of FTIR, SEM, TGA, and UTM. FTIR results showed the presence of signature peak of Si—O—Si at 1102 and 1088  $\text{cm}^{-1}$  for ENR/PVC/SiO<sub>2</sub> and ENR/PVC/TEOS membrane, respectively. Morphological studies showed that pores developed in ENR/PVC/TEOS membranes were more homogenous as compared to ENR/PVC/SiO<sub>2</sub> membranes. Thermal and mechanical stability of the membranes improved with the incorporation of silica. ENR/PVC/SiO<sub>2</sub> membrane exhibited better mechanical and thermal properties as compared to ENR/PVC/TEOS membranes. CO<sub>2</sub> and N<sub>2</sub> gas permeation of silica-filled membranes increased with increasing silica content and the permeability of ENR/PVC/SiO<sub>2</sub> membrane toward N<sub>2</sub> and CO<sub>2</sub> gasses was higher than ENR/PVC/TEOS membrane. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2013

**KEYWORDS:** membranes; composites; properties and characterization

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### INTRODUCTION

In recent years, membrane technologies have emerged as a viable and cost effective treatment alternative to treat water, wastewater, and air pollution. Membrane process is preferable over conventional techniques because it involves fewer treatment unit process, less or no chemical addition, consumes low energy, forms no harmful by-product and yet very effective and selective. The output must be complied with the increasingly stringent regulations and standards.<sup>1,2</sup> This has resulted in the increased applications of membrane process such as microfiltration, ultrafiltration, reverse osmosis, hemodialysis, and gas separation in various industries.<sup>1,3–5</sup>

Membranes can be made from organic (polymer) and inorganic (ceramic) materials.<sup>1</sup> Ceramic membranes have comparatively high chemical, mechanical and thermal resistance but very expensive, brittle, and poor membrane forming ability. Polymeric membranes are widely used because of the separation ability, flexibility, and low-cost but with disadvantages such as low chemical, mechanical, and thermal resistance.<sup>6</sup> To improve the stability of the polymeric membrane, the thin and brittle selective film is usually fabricated on a porous and robust support.<sup>1</sup> Numerous organic polymers such as polyvinylchloride (PVC),

cellulose acetate (CA), polysulfone (PSf), polyacrylonitrile, polyvinylidene fluoride (PVDF), polyether imide, and polyimide can be prepared by phase inversion method to form membranes.

In recent years, hybrid organic/inorganic composite membranes have been growing rapidly. The organic/inorganic membranes can be made by incorporating the inorganic fillers (e.g., zeolites, silica, alumina, titania, and others) into the polymer matrix.<sup>7,8</sup> The development of organic/inorganic membranes has been conducted to advance the performance of gas separation membranes. Sadeghi et al.<sup>7</sup> investigated the effect of silica nanoparticles addition on the gas separation properties of ethylene vinyl acetate. The incorporation of silica nanoparticles increases the permeability of carbon dioxide with slight changes to the selectivity. Increasing the amount of silica substantially increases the permeability of the gas. Wahab et al.<sup>9</sup> made a similar observation whereby the inclusion of nanosized fumed silica as fillers was found to enhance the carbon dioxide permeability in PSf membrane.

Being the most industrialized polymer, PVC, a thermoplastic, is an outstanding material suitable for membrane fabrication because of its stiffness, low cost, excellent physical, and chemical properties, acids, alkalines, and solvents resistance, as well as

mechanical properties.<sup>10</sup> The blend of PVC, the thermoplastic with other polymers could improve the PVC membranes performances.<sup>11,12</sup> Epoxidised natural rubber (ENR) is a good elastomer because of its hydrophilicity, high shearing and flexibility.<sup>13,14</sup> Ibrahim and Dahlan<sup>14</sup> reported that PVC has strong mechanical properties and good interaction with ENR. However, a PVC-dominant blend does not seem capable of retaining tensile strength and at certain curing temperature the blend becomes more glass-like, that is, stiffer and brittle and consequently loses most of its mechanical properties. Therefore, in this study ENR was blended in dominant to produce a flexible and mechanically tough matrix that is suitable for fabrication of a self-supporting membrane. The mechanical stability of the membrane is enhanced with the addition of silica (SiO<sub>2</sub>) into the polymer blend matrix. Silica has shown to interact to ENR/PVC due to the presence of epoxy group in ENR.<sup>15</sup> Besides, the addition of silica in the ENR/PVC matrix will help to create pores and at the same time acts as filler to improve the thermal and mechanical properties of the membrane.<sup>4,16–18</sup> Silica exists in many forms and sizes. Silica nanoparticle can be prepared through sol–gel process under repeated hydrolysis and condensation steps of silica precursor [e.g.: Tetraethoxysilane (TEOS)] in appropriate chemical conditions.<sup>16,19</sup> Arthanareeswaran et al.,<sup>4,6</sup> had found that addition of zirconia (ZrO<sub>2</sub>) and microsilica (SiO<sub>2</sub>) in CA membrane caused porosity and mechanical stability of CA/SiO<sub>2</sub> to increase. Chen et al.<sup>20</sup> had reported the *in situ* generated nanosilica acted as pore forming agent that enhanced the permeability and hydrophilicity of the membrane.

Phase inversion is a versatile technique for fabrication of porous membrane that transforms a polymer under controlled manner from liquid to solid state.<sup>20</sup> The concept of phase inversion covers wide range of techniques like solvent evaporation, precipitation by controlled evaporation, thermal precipitation, precipitation from the vapor phase and immersion precipitation. Some researchers applied phase inversion technique to fabricate organic–inorganic membrane by directly blending the prepared inorganic nanoparticles with the polymers into the membrane casting solution.<sup>6,21–23</sup> Chen et al.<sup>20</sup> proposed a method of incorporation of the *in situ* generation of inorganic nanoparticle (silica) in the CA membranes fabrication. In the method, silica nanoparticles were instantly diffused into the coagulation bath during the phase inversion process and the spaces left turned into pores by the silica on the membrane.

In this study, the ENR/PVC/silica membrane was prepared by adding two different sizes of silica; microsilica (SiO<sub>2</sub> powder) and nanosilica (generated from TEOS), into a 60 : 0 wt % of ENR/PVC blend. The effects of silica on the membrane morphology, stability and gas permeability were studied and discussed.

## EXPERIMENTAL

### Materials

ENR-50 and Polyvinyl chloride (PVC) were supplied by Malaysia Rubber Board and Sigma Aldrich respectively. Tetrahydrofuran (THF), toluene, hydrochloric acid (HCl), tetraethoxyorthosilane (TEOS), and microcrystalline silica powder (0.007 μm) were purchased from System.

### Preparation Methods

**ENR/PVC Matrix.** ENR/PVC matrix (60/40 wt %) was prepared by melt blending in an internal mixer (Brabender Plasticoder-PL 2000) at 160°C and a mixing rate of 50 rpm for 13 min. The matrix was swelled and dissolved in a mix solvent, 97.5% THF and 2.5% toluene by volume at the matrix to solvent ratio 1 : 8 (w/v) for 24 h. The ENR/PVC solution was continuously stirred for another 24 h using magnetic stirrer for homogenization.

**Preparation of ENR/PVC Matrix.** The ENR/PVC solution was deaerated for about 30 min spread on the surface of deionized water by using a syringe. 4 mL of the polymer solution spread into a thin film of about 50 cm<sup>2</sup> due to surface tension. The syringe was held sufficiently close on the water surface to minimize disturbances (e.g.: air, dust, and vibration). The phase inversion process occurred instantaneously for 30 min until the film solidified into a nontransparent membrane. The prepared membrane was collected, rinsed and dried at room temperature.

**Preparation of ENR/PVC/SiO<sub>2</sub> Membrane.** Microcrystalline SiO<sub>2</sub> powder, about 5 wt % was added into the ENR/PVC solution and homogeneously stirred for another 24 h. The ENR/PVC/SiO<sub>2</sub> membrane was prepared according to the previous method.

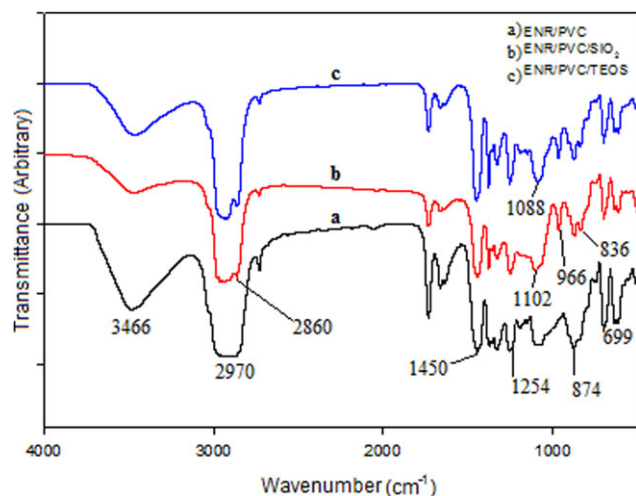
**Preparation of ENR/PVC/TEOS Membrane.** TEOS and water in the molar proportions of 1 : 2 was added to the ENR/PVC solution homogeneously stirred for 24 h. The solution was then spread on HCl solution (pH 1) for the *in situ* generation of silica nanoparticle through sol–gel process. pH 1 was chosen to reduce agglomeration of silica as at pH ≥ 2, silica particles tend to form agglomerated structures in the hybrid composite.<sup>15</sup>

**Characterization.** A Perkin Elmer Fourier Transform Infrared Spectroscopy, (GX FTIR System), was used to determine the surface functional groups of the membrane. The morphology of surface and cross section of the membranes were observed using scanning electron microscope, SEM (LEO 1450VP). The membranes were fractured in liquid nitrogen and sputter coated with gold to provide conductivity to the surface. Thermal gravimetric analysis was carried out using a Mettler Toledo thermogravimetric analyzer (TGA/SDTA 851). The analysis were performed under nitrogen atmosphere over temperature range of 50–600°C at the heating rate of 10°C/min. Tensile properties of the membranes were determined using Universal Testing Machine (Instron 5566) at cross-head speed of 50 mm/min. Dumbbell shaped were cut out of each membrane. Measurement was done according to the standard method, ASTM D 412. All membranes were air dried prior to analysis.

**Gas Permeation Test.** The permeability of carbon dioxide (CO<sub>2</sub>) and nitrogen (N<sub>2</sub>) gasses are measured using constant pressure/variable volume technique at 2, 4, and 6 psi pressures at room temperature.<sup>7</sup> The gas permeability of membranes was determined using the following equation:

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

where  $P$  is the permeability (cm<sup>2</sup>/s·cmHg),  $q$  is the flow rate of the permeate gas passing through membrane (cm<sup>3</sup>/s),  $l$  is the membrane thickness (cm),  $p_1$  and  $p_2$  are the pressures of feed



**Figure 1.** FTIR spectra for (a) ENR/PVC, (b) ENR/PVC/SiO<sub>2</sub>, and (c) ENR/PVC/TEOS membranes. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

and permeate sides (cmHg), respectively, and  $A$  is the effective area of the membrane (cm<sup>2</sup>).

The selectivity,  $\alpha$  of the membranes was calculated from pure gas experiments:

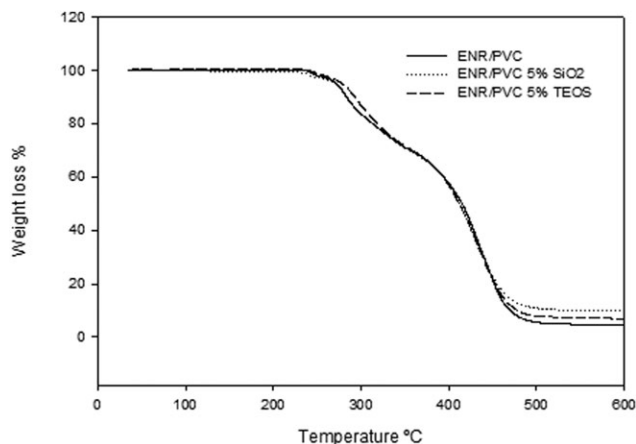
$$\alpha = P_{CO_2} / P_{N_2} \quad (2)$$

## RESULTS AND DISCUSSION

### Chemical Properties

Figure 1 shows the FTIR spectra of ENR/PVC, ENR/PVC/SiO<sub>2</sub>, and ENR/TEOS membranes. All membranes share similar absorptions in the range of 3000–2800 cm<sup>-1</sup> attributed to C-H stretching and 1450 cm<sup>-1</sup> to C-H bending. The bands at 1254, 874, and 699 cm<sup>-1</sup> are assigned to asymmetric vibration of C—O—C, C—O—C (epoxy ring) vibration, and C—Cl of PVC, respectively.<sup>15</sup>

The presence of silica in both ENR/PVC/SiO<sub>2</sub> and ENR/PVC/TEOS membranes is shown by the presence of Si—O—Si asymmetric stretching at the absorption peaks of 836 cm<sup>-1</sup>.<sup>22</sup> Furthermore, the silanol (Si—OH) absorption peak in both membranes is also detected at 966 cm<sup>-1</sup>.<sup>22</sup> The intensity of C—O—C absorption at 874 cm<sup>-1</sup> for ENR/PVC/SiO<sub>2</sub> and ENR/PVC/TEOS membranes is less than ENR/PVC membrane. According to Bandyopadhyay et al.,<sup>15</sup> the decrease in intensity of C—O—C group vibration at 874 cm<sup>-1</sup> for both silica filled membranes was probably due to the reduction of the C-O-C group concentration. This might be as a result of possible chemical interaction occurring between the silanol moieties. The overlapping of wide adsorption of C—O symmetric stretching vibrations of ENR in the range of 1110–1000 cm<sup>-1</sup> with the Si—O—Si symmetric stretching vibrations causes strong absorptions to occur at 1102 cm<sup>-1</sup> for ENR/PVC/SiO<sub>2</sub> membrane and 1088 cm<sup>-1</sup> for ENR/PVC/TEOS, respectively. Peak at 3466 cm<sup>-1</sup> indicates the presence of OH functional group. The absorption at peak 3466 cm<sup>-1</sup> for both ENR/PVC/SiO<sub>2</sub> and ENR/PVC/TEOS are

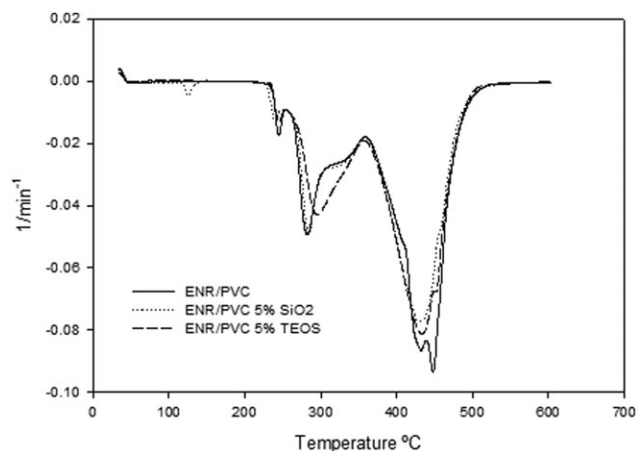


**Figure 2.** TGA curve of (a) ENR/PVC, (b) ENR/PVC/SiO<sub>2</sub>, and (c) ENR/PVC/TEOS membranes.

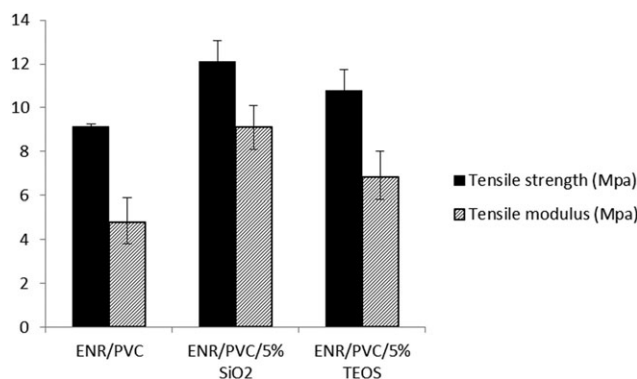
less prominent and as compared to ENR/PVC membrane. This might be due to the interaction of the matrix with the added silica.

### Thermal Properties

Figures 2 and 3 display the TGA and DTG curves of ENR/PVC, ENR/PVC/SiO<sub>2</sub>, and ENR/PVC/TEOS membranes, respectively. Two distinctive degradation stages are clearly shown. The first degradation stage occurs in the range of 250–350°C corresponding to the degradation of PVC matrix<sup>24</sup> while the second degradation stage in the range of 370–500°C can be ascribed to the decomposition of polyisoprene chain in ENR.<sup>25</sup> The residue of the ENR/PVC, ENR/PVC/TEOS, and ENR/PVC/SiO<sub>2</sub> membranes are 4.6, 6.9, and 9.8%, respectively. Although the initial silica added was 5 wt %, but the silica remained is expected to be less as some of the silica will be leached out from the membrane during the phase inversion process depending on the interaction of the silica with the polymer matrix and the affinity of silica toward water. As silica decomposes at higher temperatures, no degradation of silica will be expected at 600°C. This indicates the incorporation of the silica moiety into the polymer



**Figure 3.** DTG curve of (a) ENR/PVC, (b) ENR/PVC/SiO<sub>2</sub>, and (c) ENR/PVC/TEOS membranes.



**Figure 4.** Mechanical study of (a) ENR/PVC, (b) ENR/PVC/SiO<sub>2</sub>, and (c) ENR/PVC/TEOS membranes.

matrix resulted in the improvement of thermal stability of the polymer.

In DTG curves (Figure 3), all the membranes exhibit a similar decomposition peaks. A slight endothermic peak around 100°C is caused by the dehydration of water content of the membrane. As stated in Figure 2, the region of 250–350°C belongs to the decomposition of PVC. At this region, ENR/PVC/SiO<sub>2</sub> membrane shares the same degradation pattern with the ENR/PVC membrane. In ENR/PVC/TEOS membrane, the peaks shifted to the higher temperature. The decomposition temperature for ENR/PVC/TEOS membrane was 300°C (from the endothermic peak) which is higher than ENR/PVC (285°C) and ENR/PVC/SiO<sub>2</sub> (286°C) membranes showing that ENR/PVC/TEOS membrane exhibited good thermal stability than the others. In the ENR decomposition region, the ENR degradation peak of unfilled ENR/PVC membrane shows two distinctive peaks. Two types of ENR chain is implied which might be due to the attachment of ENR to branched PVC or the attachment of ENR with linear PVC. In the presence of silica, the shape of the band changes into a single peak. Strong polymer and silica interaction has reduced the different type of chains into a single moiety. Silica has a stronger interaction with ENR than PVC component due to the presence of epoxide group in ENR. The interaction of silica with the ENR/PVC matrix enhances the thermal stability of the membranes.

### Mechanical Properties

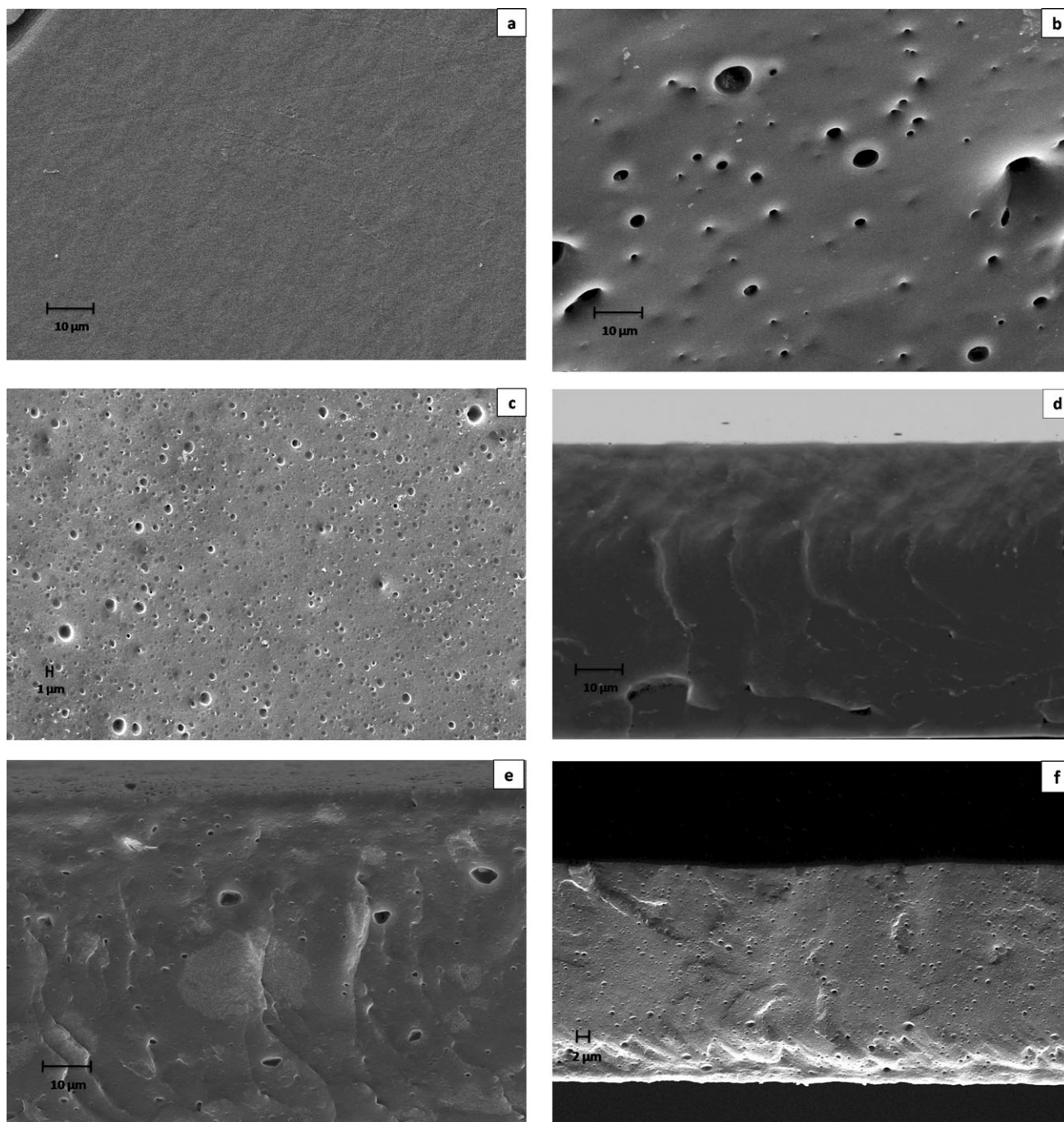
The results of mechanical studies of each membrane are shown in Figure 4. The tensile strength and modulus of the ENR/PVC has improved after addition of SiO<sub>2</sub> and TEOS. ENR/PVC, ENR/PVC/SiO<sub>2</sub>, and ENR/PVC/TEOS exhibit tensile strength of 9.1, 12.1, and 10.76 MPa, respectively, while the respective tensile modulus are 4.8, 9.1, and 6.8 MPa of modulus value. The average thickness of all the membranes was  $77 \pm 6 \mu\text{m}$ . A similar observation has been reported by Arthanareeswaran et al.<sup>6</sup> who stated that at the optimum addition of silica particles, the macrovoids suppression and interaction between inorganic particles and polymer matrix, result in increasing the mechanical strength of membrane.

It also can be seen that ENR/PVC/SiO<sub>2</sub> membrane exhibited higher tensile strength than ENR/PVC/TEOS membrane.

Incorporation of filler into a polymer matrix may increase or decrease the mechanical properties of composites depending on the amount and dispersion of the filler added.<sup>26</sup> As mentioned previously, the amount of silica in the polymer matrix is less than the initial amount added. ENR/PVC/TEOS membrane exhibits a lower mechanical property than ENR/PVC/SiO<sub>2</sub> is probably due the amount of nanosilica loss during phase inversion is higher than microsilica. Bigger particles of silica create higher interaction between them and have prone to diffuse into the nonsolvent. Small aggregates of nanoparticles have a particle interaction with the polymer matrix and have more probable to diffuse into the nonsolvent during the phase inversion process. Incomplete hydrolysis of TEOS also might lead in reducing the generated silica amount. This is supported by the residual weight of ENR/PVC/SiO<sub>2</sub> (9.8%) is greater than ENR/PVC/TEOS (6.9%). The good interaction between microsilica and the ENR/PVC matrix as shown by the TG and DTG analyses contribute to the increment of the properties. The ENR/PVC/SiO<sub>2</sub> membrane also exhibits high modulus compared to other membranes since the addition of microsilica increases the stiffness of the membrane. According to Yu et al.<sup>16</sup> and Ogoshi et al.,<sup>27</sup> SiO<sub>2</sub> could act as point of crosslinking in composite membranes to link the polymer chains and thus increases the polymer chain rigidity thus more energy is needed to break down the bond between filler and the polymer matrix, resulting in the improved mechanical strength of the membranes. Yu et al.<sup>16</sup> made similar observation regarding the mechanical stability for PVDF-SiO<sub>2</sub> membranes. Further, Arthanareeswaran et al.<sup>6</sup> also found the increased mechanical stability in terms of tensile intensity, tensile stress and elongation at break for CA membrane with SiO<sub>2</sub>. Silica in the membrane acts as a filler to improve the mechanical properties of the membranes.

### Membrane Morphology

Figure 5 indicates the SEM images of the surface and cross-section of the membranes. Pore development is clearly seen in ENR/PVC/SiO<sub>2</sub> [Figure 5(b,e)] and ENR/PVC/TEOS [Figure 5(c,f)] membranes as compared to the smooth ENR/PVC membrane [Figure 5(a,d)]. The pore size was determined via visual examination using scanning electron microscopy. It was found that the average pore size of the ENR/PVC/SiO<sub>2</sub> was in the range of 7.6–19.2  $\mu\text{m}$  whereas the average pore size of the ENR/PVC/TEOS was in the range of 30–130 nm. The affinity of silica toward water result in some of the silica particles to diffuse into water bath and leaving pores in the membrane.<sup>6,20</sup> In other words, when the polymer solution is dropped onto the water surface, some of the silica diffuses into the water, while the membrane undergoes curing. The voids left by the silica particles develop into pores. Larger pores are generated in ENR/PVC/SiO<sub>2</sub> membrane as a result of the size of microsilica and its agglomerates. Conversely, smaller pores are created in ENR/PVC/TEOS membrane due to the size of nanosilica hydrolyzed from TEOS. Microsilica disrupts the polymer chain segments greater than nanosilica, thus, increases the free volume between the polymer chains and produces bigger pores.<sup>28</sup> Furthermore, the development of pores might also occur during the diffusion of the solvent to the surface of the membrane and evaporate



**Figure 5.** SEM images of surface of (a) ENR/PVC, (b) ENR/PVC/SiO<sub>2</sub>, (c) ENR/PVC/TEOS, and cross-section of (d) ENR/PVC, (e) ENR/PVC/SiO<sub>2</sub>, (f) ENR/PVC/TEOS membranes at  $\times 1000$  magnification.

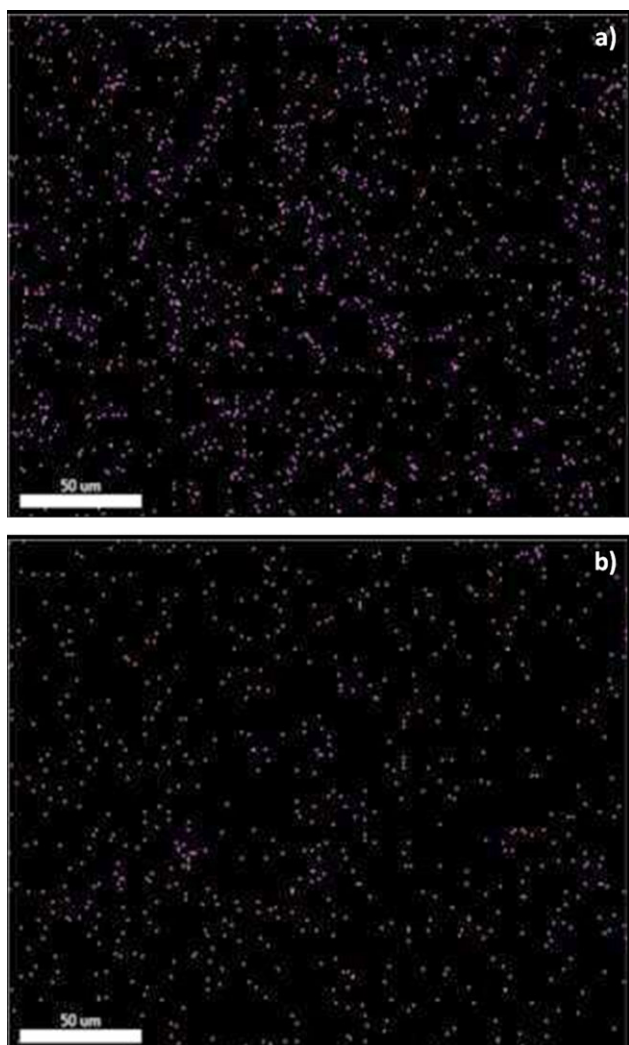
from the surface contacted to air and the remaining solvent exchanged with the water from the water bath.<sup>29</sup>

The distribution of the pores in the ENR/PVC/TEOS membrane is better than in the ENR/PVC/SiO<sub>2</sub> membrane. This is highly related to the distribution of the silica particles in the matrix as can be seen from the EDX mapping in Figure 6. The distribution of silica in the ENR/PVC/TEOS membrane is more homogeneous than in ENR/PVC/SiO<sub>2</sub> membrane. Agglomerated silica structures are relatively higher in ENR/PVC/SiO<sub>2</sub> membrane

since microsilica was added during membrane solution mixing. Although for TEOS, generation of nanosilica occurred during phase inversion process throughout the membrane.

#### Gas Permeation

Figure 7 presents the permeability of ENR/PVC, ENR/PVC/SiO<sub>2</sub>, and ENR/PVC/TEOS membranes toward carbon dioxide gas (CO<sub>2</sub>) and nitrogen gas (N<sub>2</sub>) through. The permeability of both gasses increases with pressure which is common with a pressure-driven membrane. The permeation of both gases

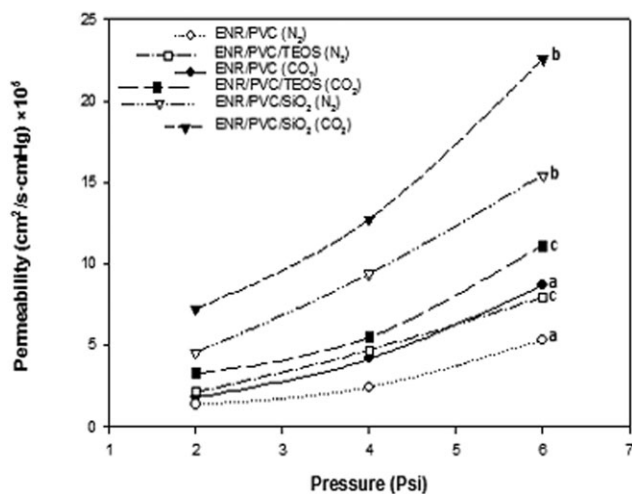


**Figure 6.** EDX silicon mapping of (a) ENR/PVC/SiO<sub>2</sub> and (b) ENR/PVC/TEOS membranes.

through ENR/PVC/SiO<sub>2</sub> is the highest followed by ENR/PVC/TEOS and ENR/PVC membranes. This is due to the relative size of the pore in the membrane where the order is ENR/PVC/SiO<sub>2</sub> > ENR/PVC/TEOS > ENR/PVC.

The permeability of CO<sub>2</sub> gas is relatively greater than that of N<sub>2</sub> gas for all membranes. N<sub>2</sub> gas is considered to be a noninteracting gas whereas CO<sub>2</sub> gas interacts with the membrane. According to Wahab et al.,<sup>9</sup> CO<sub>2</sub> gas has high interaction with silica because of the OH (hydroxyl) functional group on the silica particles (as confirmed by FTIR spectrum in Figure 1). This can be attributed to an increased solubility of CO<sub>2</sub> in the membrane. Thus, the incorporation of silica into the polymer matrix makes a major contribution to enhance solubility and accordingly improve the diffusivity of CO<sub>2</sub> gas in the membranes.<sup>28</sup> Sadeghi et al.<sup>7</sup> also discussed that CO<sub>2</sub> gas is easily diffused in the silica-filled membrane. Furthermore, since the size of the pores of the ENR/PVC/SiO<sub>2</sub> is greater than those of ENR/PVC/TEOS, the diffusivity is higher.

The selectivity of CO<sub>2</sub>/N<sub>2</sub> of each membranes is calculated in Table I. The selectivity of CO<sub>2</sub>/N<sub>2</sub> increases with the permeabil-



**Figure 7.** Permeability of CO<sub>2</sub> and N<sub>2</sub> in (a) ENR/PVC, (b) ENR/PVC/SiO<sub>2</sub>, and (c) ENR/PVC/TEOS membranes.

ity of gas in ENR/PVC membrane. ENR/PVC shows higher CO<sub>2</sub>/N<sub>2</sub> selectivity followed by ENR/PVC/SiO<sub>2</sub> and ENR/PVC/TEOS membranes. According to Scholes et al.,<sup>30</sup> a high permeable membrane tends to have low selectivity. Selectivity of CO<sub>2</sub>/N<sub>2</sub> decreases as permeability increases due to the formation of free volume (pores). The value of selectivity for all membranes is greater than unity. This was because CO<sub>2</sub> (3.3 Å) has a smaller kinetic diameter than N<sub>2</sub> (3.64 Å).<sup>1,30</sup> So, smaller gas molecules will diffuse at a much faster rate than larger gas molecules.

## CONCLUSIONS

Porous membrane made of ENR/PVC can be prepared using phase inversion technique. Large pores were found with the addition of microsilica (SiO<sub>2</sub> powder) whereas small pores formed with the *in situ* generated nanosilica (TEOS). Thermal and mechanical stability of the membranes improved with the addition of silica. The ENR/PVC/SiO<sub>2</sub> showed higher residue of 9.8% compared to ENR/PVC/TEOS and ENR/PVC membranes. The mechanical stability of the ENR/PVC/SiO<sub>2</sub> also exhibited higher tensile strength and modulus compared to ENR/PVC/TEOS membrane. The pores in ENR/PVC/TEOS membrane were homogenous in distribution than in ENR/PVC/SiO<sub>2</sub> membrane due to the size of the silica. The silica-filled membranes showed an increase in CO<sub>2</sub> gas and N<sub>2</sub> gas permeability upon increasing silica content. ENR/PVC/SiO<sub>2</sub> membrane exhibited higher CO<sub>2</sub> gas permeability over ENR/PVC/TEOS membrane due to the pore size and interaction of CO<sub>2</sub> gas with silica.

**Table I.** CO<sub>2</sub>/N<sub>2</sub> Selectivity Coefficient of (a) ENR/PVC, (b) ENR/PVC/SiO<sub>2</sub>, and (c) ENR/PVC/TEOS Membranes

Pressure (Psi)	ENR/PVC	ENR/PVC/SiO <sub>2</sub>	ENR/PVC/TEOS
2	1.33	1.60	1.54
4	1.70	1.35	1.17
6	1.63	1.46	1.39

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