

Fabrication, Characterisation, and Pervaporation Performance of Graphene/Poly(Vinyl Alcohol) Nanocomposite Membranes for Ethanol Dehydration

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Malic acid cross-linked poly(vinyl alcohol)/graphene (MA-PVA/Ge) nanocomposite membranes were fabricated by solution-casting method. The effects of PVA, MA, and Ge concentrations on pervaporation (PV) performance of membranes for dehydration of 80 wt% ethanol solution were investigated. The membrane characterisations were performed by atomic force microscopy, transmission electron microscopy, Fourier-transform infrared spectroscopy, X-ray diffraction, tensile testing, differential scanning calorimetry, swelling degree, and water contact angle. The characterisation and PV results indicated that the thermal stability, swelling degree, and separation performance of MA-PVA/Ge nanocomposite membrane were improved compared to neat PVA by adding 10 wt% PVA solution with 20 wt% MA and 0.15 wt% Ge in respect to the weight of PVA (20MA-10PVA/0.15Ge). This membrane exhibited good PV performance with a good selectivity of 596, an equivalent permeate flux of 0.12 kg/m²h, and a high PV separation index of 68.4 kg/m²h for dehydration of 80 wt % ethanol concentration in the feed solution (C_F) at feed temperature (T_F) of 50 °C, feed flow rate of 60 L/h, and vacuum pressure (P_V) of -100 kPa.

1. Introduction

Ethanol is considered to be the most promising fuels of the future since it is obtained from renewable sources (He et al., 2012). Traditional methods for separating azeotropic mixture to obtain absolute ethanol include desiccation, using adsorbents, as well as azeotropic distillation and extractive distillation or vacuum distillation. In recent years, membrane technology could be applied (Frolkova et al., 2010). Pervaporation (PV), a binary or multi-component liquid mixture is separated by partial evaporation via a dense membrane (Barker, 2014).

Poly(vinyl alcohol) (PVA) is a possible candidate. PVA must be modified to minimise the swelling in water when fabricated for the dehydration of ethanol solution. This can reduce its selectivity in the ethanol dehydration by PV, though PVA proved to be a satisfactory permeation flux. Cross-linking is a way to prevent this drawback of PVA (Yamasaki et al., 1995). The decrease in crystallinity was important (Peng et al., 2011). Malic acid (MA) is considered to be a right choice due to a more effective cross-linking and a superior water permeability in comparison to others (Peng et al., 2011). Enhancement the PV performance has been achieved by adding nanofillers into the polymer matrix (Ravindra et al., 2015).

In this study, MA cross-linked PVA/Ge nanocomposite membranes with a different loading content of PVA, MA, and Ge were prepared to investigate the PV performance of membranes for dehydration of ethanol solution.

2. Experimental

2.1 Materials

PVA (MW 80,000 and > 98 %), sulfuric acid (98 wt%), sodium nitrate (99 wt%), hydrogen peroxide (30 wt%), hydrazine hydrate (35 wt%), and MA (99 wt%) were purchased from Xilong Chemical, China. Graphite

(particle size: < 50 μm , density: 20 - 30 g/100 mL) was purchased from Sigma Aldrich, Germany. Potassium permanganate (> 99.5 wt%) and ethanol (96 vol%) were purchased from ViNa Chemsol, Vietnam. All chemicals were used without any further purification.

2.2 Membrane fabrication

Ge was synthesised from graphite by a modified Hummers' method. 0.05 g of Ge was dispersed in deionised water and sonicated for 24 h to obtain Ge suspension. According to the solution-casting method, 10 g of PVA was dissolved in deionised water and heated at 90 °C to form 10 wt% PVA solution. Then, 20 wt% (respect to the weight of PVA) of a cross-linking MA was gradually added. The solution was stirred for 5 h at 90 °C to completely cross-linked reaction. Next, 12 mL of Ge aqueous suspension corresponding to 0.15 wt% (based on the weight of PVA) was dropped into MA cross-linked PVA solution, and stirred for 1 h. The obtained homogeneous solution was casted on petri dish and dried at room temperature for 24 h to form the nanocomposite membrane. Finally, the membrane continued to be dried at 80 °C for 4 h to constant weight. The nanocomposite was denoted 20MA-10PVA/0.15Ge, corresponding to PVA, MA and Ge content of 10, 20, and 0.15 wt%.

2.3 Characterisation

Atomic force microscopy (AFM) measurement was performed on an AFM Nanotech Electronica by casting powder dispersion onto freshly cleaved mica substrates and drying under ambient condition. Transmission electron microscopy (TEM) images were taken by JEM-1400 machine with an accelerating voltage of 100 kV. Fourier-transform infrared spectroscopy (FTIR) spectra were obtained in the range of wavenumber from 4,000 cm^{-1} to 500 cm^{-1} during 64 scans on Alpha-E Bruker (Bruker Optik GmbH, Ettlingen, Germany) spectrometer. X-ray diffraction (XRD) patterns were obtained by Advanced X8, Bruker (German) with $\lambda = 0.154$ nm, step of 4°/min from 10° to 40°. Tensile testing was performed with AND RTC 1210A (Tensilon, Japan), carried out under initial tensile length of 40 mm, drawing speed of 50 mm/min, and making use of a 1,000 N load cell. Differential scanning calorimetry (DSC) was performed with DSC-1 (Mettler Tolado, America) differential scanning calorimeter in the temperature range of from -50 °C to 250 °C. Swelling degrees (S) were carried out by immersing in deionised water at room temperature at least 48 h to reach absorption equilibrium, and were calculated as follows:

$$S = \frac{W_S - W_D}{W_D} \times 100\% \quad (1)$$

where W_S and W_D are the weight of swollen and dry membrane.

Water contact angles measurements were assessed by a OCA20 contact angle meter equipped with an image capturing system. Static contact angles were measured by the sessile drop method.

2.4 Pervaporation experiment

A laboratory scale PV unit is shown in Figure 1. The membrane was placed on the stainless screen support in the module, with the effective surface area of 28.3 cm^2 . An aqueous ethanol of 80 wt% was used as feed solution. During the experiment, the feed solution was heated up to 50 °C and circulated through the membrane module from the feed tank. The pressure on the permeate side of membrane was kept at -100 kPa via a vacuum pump. The permeate vapour was collected in cold trap at -20 °C. For each experiment, the operating time was at least 2 h to ensure that a steady state was reached. The collected permeate in cold trap was weighted to calculate the permeate flux and measured the concentration by a refractometer to determine the selectivity. The performance of PV was expressed by permeate flux (J), selectivity (α), and PV separation index (PSI), as follows (Bruggen et al., 2015):

$$J = \frac{1}{A} \frac{\Delta W}{\Delta t} \quad (2)$$

$$\alpha = \frac{y_{H_2O} / y_{C_2H_5OH}}{x_{H_2O} / x_{C_2H_5OH}} \quad (3)$$

$$PSI = J(\alpha - 1) \quad (4)$$

where ΔW (kg) is the weight of permeate during the experimental time Δt (h), A (m^2) is the effective membrane area; and x , y are the mass fraction of either water or ethanol in the feed and the permeate.

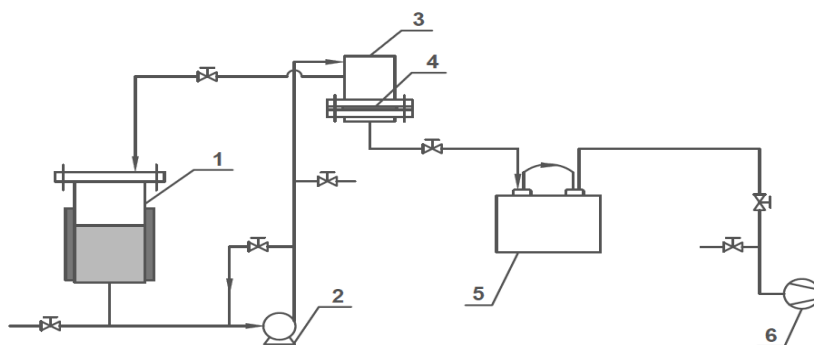


Figure 1: Schematic diagram of PV system. (1. Feed tank, 2. Metering pump, 3. Membrane module, 4. Membrane, 5. Cold trap, 6. Vacuum pump)

3. Results and discussion

3.1 Effect of PVA, MA, and Ge concentrations on pervaporation performance of membranes

3.1.1 PVA concentration

The effect of PVA concentration on the membrane performance are presented in Figure 2. Membrane selectivity increased while the permeation flux decreased (Hieu et al., 2016). However, the selectivity hardly increased when concentration of PVA was over 10 wt%. This can be explained as the free volume of water transferring channels have reached a limit value, which led to an insignificant changeability of the membrane's selectivity. This phenomenon is in accordance with previous researches (Hieu et al., 2016). PSI is defined as a parameter to evaluate the performance of the overall PV process (Bruggen et al., 2015). As observed in Figure 2, at 10 wt% concentration, PVA membrane exhibited the highest PSI with a high permeate flux of 0.22 kg/m²h and an equivalent selectivity of 28.7. This result indicated that PVA concentration of 10 wt% was a reasonable value for membrane fabrication.

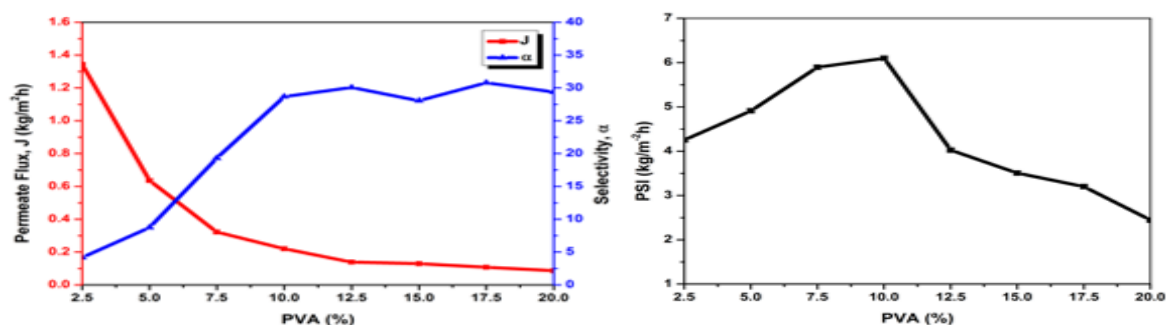


Figure 2: Effect of PVA concentration on J, α , and PSI

3.1.2 MA concentration

Nanocomposite membranes presented higher selectivity but lower permeate fluxes than that of neat PVA when MA contents were less than 20 wt% (Figure 3). The phenomenon showed in contrast when the MA contents are higher than 20 wt%. This can be due to the crystallinity and hydrophilicity which may affect each other. The crystallinity and hydrophilicity will decrease with the increase in density of cross-linking (Peng et al., 2011).

3.1.3 Ge concentration

Effect of different Ge loading on PV performance of membranes is shown in Figure 4. At a low loading level (≤ 0.15 wt%), Ge nanosheets were well-dispersed into and obtained stable structure PVA chains. This is in agreement with the initial theoretical prediction of Ge nanosheets's acting as molecular sieves that help to reject large particles, such as ethanol, after they were dispersed into the PVA matrix (Lee et al., 2013).

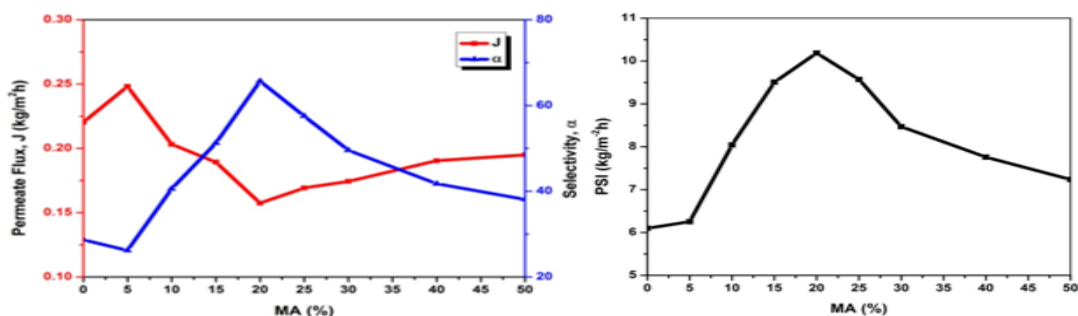


Figure 3: Effect of MA content on J , α , and PSI

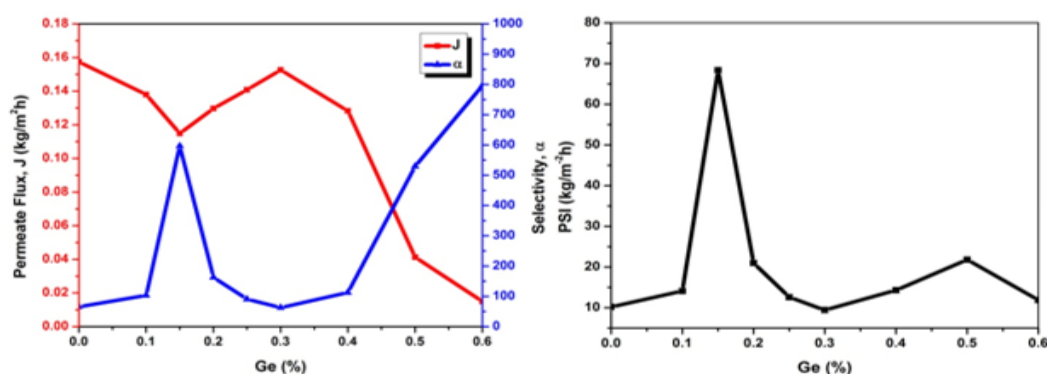


Figure 4: Effect of Ge loading content on J , α , and PSI

3.2 Characterisation

3.2.1 AFM and TEM images

AFM image and height profile for Ge are as shown in Figure 5. This result confirmed that Ge sheets were successfully synthesised with an average thickness of 0.953 nm. In order to evaluate the dispersion of Ge sheets in the PVA matrix, the ultrathin sections of membrane were observed *via* Figure 6. A homogeneous dispersion and alignment of Ge in PVA that obtained dark lines with the average thickness of 5 - 20 nm was observed in Figure 6.

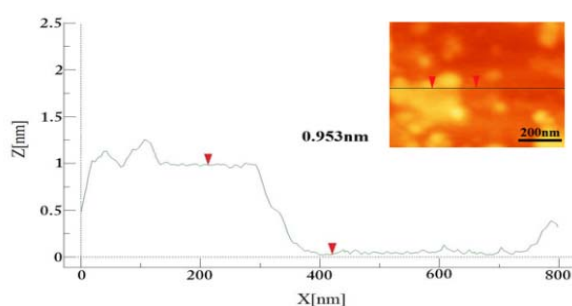


Figure 5: AFM image and height profile of Ge

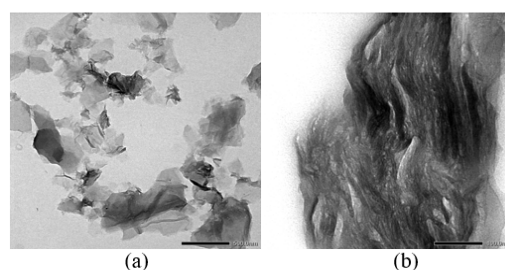


Figure 6: TEM images of (a) vertical and (b) horizontal sections of 20MA-10PVA/0.15Ge membrane

3.2.2 FTIR analysis

Figure 7 shows the FTIR spectra of 20MA-10PVA, 20MA-10PVA/0.15Ge, and neat PVA membranes. The absorptions at $3,550\text{ cm}^{-1}$ – $3,200\text{ cm}^{-1}$, $2,840\text{ cm}^{-1}$ – $3,000\text{ cm}^{-1}$, and $1,145\text{ cm}^{-1}$ are typical to the presence of $-\text{O}-\text{H}$, $-\text{CH}_2-$ (symmetric and asymmetric) and $-\text{C}-\text{O}$ groups of PVA matrix (Gohil and Ray, 2006). Compared to PVA, the spectra of 20MA-10PVA and 20MA-10PVA/0.15Ge exhibited an enhancement of the –

C=O stretching peak at $1,741\text{ cm}^{-1}$ and the decrease in the –O–H and –C–O stretching vibration, which can be identified as the formation of ester bonds between –COOH groups of MA and –OH groups of PVA chains (Bolto et al., 2009). For 20MA-10PVA/0.15Ge membrane, it is noticed that there are the same intensities of peaks as that of MA-PVA membrane.

3.2.3 Membrane crystallinity

XRD is an effective method to characterise the crystalline properties of nanocomposite. As shown in Figure 8, the peak of Ge, and neat PVA appeared at $2\theta \approx 10^\circ$ and 20° . This result demonstrated the dispersion of the Ge nanosheets into matrix and the completeness of cross-linking reaction of MA with PVA.

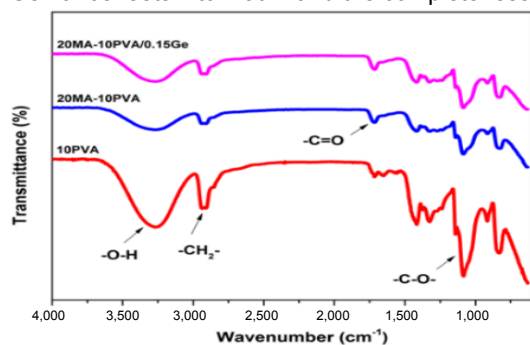


Figure 7: FTIR spectra of membranes.

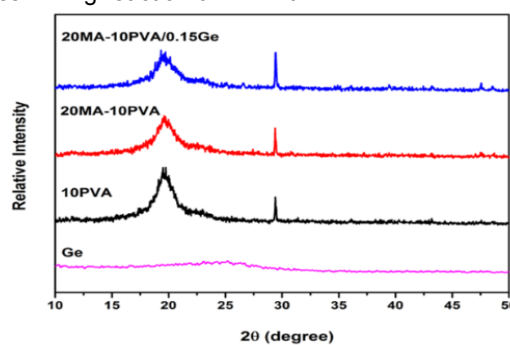


Figure 8: XRD patterns of Ge and membranes.

3.2.4 Mechanical properties

The tensile strength, T_B , and elongation at break, E_B , of PVA and nanocomposite membranes are summarised in Table 1. The decrease in T_B of composite membranes was observed. The decreasing trend of T_B confirmed the fact that the degree of crystallinity and the mechanical strength of polymer often go hand in hand, i.e., the higher the crystallinity. Further, as a matter of fact, the expense of T_B is generally on the enhancement of E_B of material (Lee et al., 2013).

Table 1: Tensile strength, T_b , elongation at break, E_B , swelling degree and water contact angles of membranes

| Membranes | T_B (MPa) | E_B (%) | Swelling degree (%) | Contact angle ($^\circ$) |
|-------------------|-------------|-----------|---------------------|----------------------------|
| 10PVA | 176.45 | 4.46 | 89 | 51.6 |
| 20MA-10PVA | 128.54 | 4.69 | 66 | 62.3 |
| 20MA-10PVA/0.15Ge | 96.36 | 4.08 | 54 | 67.5 |

3.2.5 Thermal properties

From the DSC curves as shown in Figure 9, T_g and the melt isotherm, T_m of membranes were $125 - 131\text{ }^\circ\text{C}$ and $224\text{ }^\circ\text{C}$. At the same time, new bridges are being generated between the chains through the cross-linker and the incorporation are occurring due to its acting as a nucleating agents of fillers with the chains (Lee et al., 2013).

3.2.6 Swelling degree

Table 1 shows the swelling properties of PVA and nanocomposite membranes. The presence of a large number of the hydroxyl groups in PVA results in strong hydrogen bonding, which in turn decreases the swelling of PVA in water. For 20MA-10PVA and 20-MA-10PVA/0.15Ge membranes, the swelling degree was greatly suppressed. This can be explained by cross-linking of the PVA polymer chains through the formation of ester linkages between carboxylic groups of MA and hydroxyl groups of PVA chains (Gohil and Ray, 2006).

3.2.7 Contact angle

Water contact angle results are shown in Figure 10 and Table 1. The membranes were hydrophilic. The neat PVA showed the highest hydrophilic, with a water contact angle of 51.6° . This is due to the increase in the cross-linking density of PVA via MA, and the dispersion of hydrophobic Ge sheets into PVA chains.

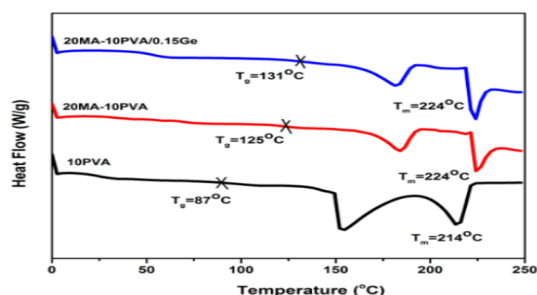


Figure 9: DSC curves of membranes

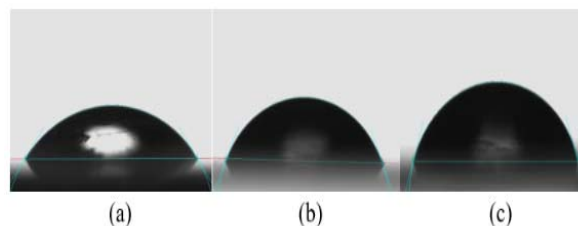


Figure 10: Photographs of water contact angles: (a) PVA, (b) 20MA-10PVA, and (c) 20MA-10PVA/0.15Ge.

4. Conclusions

A nanocomposite membrane was fabricated via a solution-casting method. Pervaporation testing results of the membrane for dehydration of 80 wt% ethanol solution demonstrated that the addition of 20 wt% MA and 0.15 wt% Ge in respect to the weight of PVA resulted in a good selectivity of 596, permeate flux of 0.12 kg/m²h, and PSI of 68.4 kg/m²h. AFM image indicated that the successfully synthesised Ge with an average thickness of 0.953 nm was obtained. TEM images revealed that Ge nanosheets dispersed into the PVA matrix to the dark lines with an average thickness from 5 - 20 nm. Tensile testing, DSC, swelling degree, and water contact angle analyses demonstrated that the characteristics of 20MA-10PVA/0.15Ge membrane were improved in comparison to PVA.

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