

Effect of Dodeca-Tungstophosphoric Acid on Morphology and Performance of Polyvinyl Alcohol Membrane for Gas Separation

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Received 7 March 2008; accepted 22 March 2009

DOI 10.1002/app.30489

Published online 8 June 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: In this article, organic/inorganic membrane was prepared for gas separation by incorporating dodecatungstophosphoric acid (PWA) into the base polymer. Flat-sheet composite membranes were produced via dry-phase inversion method. In the first stage, the effects of PWA concentration on morphology and performance of polyvinyl alcohol (PVA) membranes were elucidated. For this stage, the preparation of membranes was carried out at constant temperature of 40°C. The porosity of the prepared membrane was slightly increased with addition of PWA. By increasing the PWA concentration up to 6 wt % in the membrane recipe, the permeability of N₂, O₂, and air was improved from 50,000 (for no addition of PWA) to around 160,000, 140,000, and 80,000 L m⁻² h⁻¹, respectively. For H₂, this was enhanced from 110,000 to 230,000 L m⁻² h⁻¹. The ideal selectivity of the membrane was slightly improved for N₂/air (from 1 to 1.2). For N₂/O₂ pair, the initial drop (from 2.5 to 1.5) was followed by a slight increase (1.5–1.9). Moreover, the selectivity was decreased for H₂/air (from 2.8 to 1.8) and H₂/N₂ (from 2.2 to 1.7) by

increasing the PWA concentration. The 10 wt % PVA membrane with 6 wt % PWA demonstrated superior performance compared with the other compositions. In summary, the presence of PWA in the casting solution results in lower flux for O₂ and higher selectivity for H₂/O₂ pair. In the second stage, the effects of solvent evaporation temperature (10, 27, 40, and 80°C) on morphology and performance of the membranes were studied. By increasing the temperature, the number and size of voids were increased. The permeation of gases was improved from 100,000 L m⁻² h⁻¹ (at 10°C) to 150,000 (O₂), 250,000 (air), 380,000 (N₂), and 600,000 L m⁻² h⁻¹ (H₂) by increasing the temperature up to 80°C. This increment resulted in selectivity alteration either increment or diminishment. The selectivity was changed from 1.3 to 3.2 (H₂/O₂), 0.8–2.5 (N₂/O₂), 1.2–2.4 (H₂/air), 0.6–1.5 (N₂/air) and 2.0–1.5 (H₂/N₂). © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 484–490, 2009

Key words: membranes; morphology; gas separation; polytungstophosphoric acid; polyvinyl alcohol

INTRODUCTION

Polymeric membranes are widely used in gas separation processes.^{1–4} PVA seems an attractive material for producing membranes⁵ because of acceptable chemical, physical, mechanical, and thermal stability, biodegradability, and cost individually or as a blend.^{6–11} PVA is a water-soluble synthetic polymer with excellent film-forming capability.¹² Because of proton-exchange potential, PVA membranes have been used for proton conductivity and methanol permeability.¹³

Polyoxometalates (POMs) are inorganic molecules^{14,15} containing metal and oxygen, which are divided to the classes of isopolyanions [M_mO_y]^{p-} and heteropolyanions (HPAs) [X_xM_mO_y]^{q-}. They are

characterized by a metallic center, M, which is surrounded by some atoms or groups of atoms, and X is the heteroatom. The structure illustrated in Figure 1 was first reported by Keggin for dodeca-tungstophosphoric acid (PWA). This type of commercially available POM is widely used for various applications. The basic structural unit of PWA is the Keggin anion (PW₁₂O₄₀)³⁻, which consists of the central PO₄ tetrahedron surrounded by four W₃O₁₃ sets linked together through oxygen atoms. Each W₃O₁₃ set is formed by three-edge sharing WO₆ octahedral. They form channels that can contain up to 29 water molecules in different hydrate phases. This leads to various protonic species and hydrogen bonds of different strengths.^{16,17} Lower hydrates of PWA containing six water molecules are stable up to 180°C,¹⁶ an important property to prepare fuel cell membranes working at temperatures higher than 100°C.

HPAs are among the highly conductive and thermally stable inorganic modifiers¹⁸ with different

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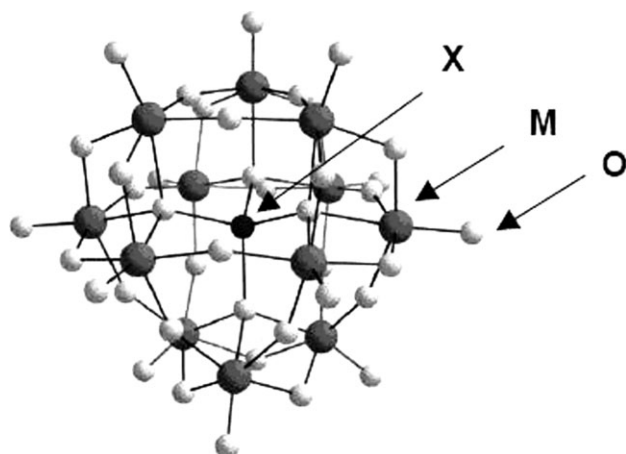


Figure 1 The Keggin structure of $[XM_{12}O_{40}]^{n-}$ anions.

hydrated structures depending on the environment.^{19,20} PWA is stable at temperatures higher than 100°C.²⁰ There is increasing interest in using the HPA as proton conducting components in fuel cells for elevated temperature operation, 120–200°C.^{18,21,22}

HPA acts as a Brønsted acid²³ with water molecules in their structure.²⁴ PWA is a form of HPA.²⁵ Contrary to the unique capabilities, there is no published report on applications of PVA/PWA hybrid membrane in H₂/O₂ fuel cells.²⁶ However, the compression-molded POM plates were employed as partition walls between anode and cathode chambers of H₂/O₂ fuel cells. POM allows selective permeation of protons from anode to cathode through hydrogen bonds facilitated by solvent molecules.²⁷ Moreover, solid forms of POMs are sorbents of gases.^{28,29} The membranes made of water-soluble organic polymers and heteropolyacids were used in gas sensors for detection of hydrogen.^{29,30} In general, the addition of PWA on PVA membrane increases the proton conductivity.^{31,32}

PVA and PWA with superior characteristics are appropriate individual components for membrane preparation. Their mixture results in an interaction between active groups of both sides affecting the membrane structure leading to alteration in membrane performance. The aim of this work was preparation and characterization of tungstophosphoric acid doped polyvinyl alcohol hybrid membranes for gas separation. PVA and PWA were selected as base polymer and additive for preparation of flat-sheet membranes. Casting solutions were prepared from PVA dissolved in water with and without the addition of PWA. The effects of PWA addition on morphology and performance of PVA membranes were elucidated. This study may be considered as a basis for membranes prepared from mixture of PVA and PWA. The membrane may be employed for separation of hydrogen and application in fuel cell for elevated temperature operation.

EXPERIMENTAL

Materials

The following chemicals were employed for preparation of membranes: PVA (hydrolysis degree equal to 98%, $M_w = 72,000$ g/mol) by Aldrich as the membrane matrix, PWA ($M_w = 2800$ g/mol) by Fluka as additive, and distilled water as solvent for PVA. Gases (H₂, N₂, O₂, and air, purity 99.999%) were used for investigating the membrane performance.

Preparation of polyvinyl alcohol membrane

The PVA membranes were prepared from ternary systems of (PVA/PWA/H₂O) via dry-phase inversion (solvent evaporation) using different concentrations of PWA in the casting solution. The wet thickness (gap between the glass plate and casting rod) was maintained at 80 μm for all membranes.

PVA was dissolved in water at 70°C for 1 h with continuous stirring. PWA was added in homogeneous solution of PVA at room temperature with continuous stirring until homogeneous solution was obtained (for about 24 h). The experiments were carried out at two stages. In the first stage, the membrane were prepared with various concentrations of PWA and constant temperature of 40°C. The amount of PWA in the membrane was changed from 2 to 6 wt %. There is a limitation for preparation of membrane with high PWA concentration (more than 6 wt%) by phase inversion due to increase in the viscosity of polymeric solution. The preparation of membranes was carried out at constant temperature of 40°C. In the second stage, the membranes were fabricated at different temperatures with constant PWA concentration. The casting film on the glass plate was kept at room temperature (27°C) or placed in fridge at 10°C or immediately placed in an oven at 40 and 80°C for around 2 h or 30 min. The effect of temperature in the phase inversion stage is among the most important parameters affecting membrane morphology.

Membrane performance

The permeability of H₂, O₂, N₂, and air through the prepared membranes (flux) and ideal selectivity of pair gases were elucidated using a special setup (Fig. 2). For measuring the permeation of gases through the membrane, a simple and low-cost technique was employed. The permeated gas through the membrane was released into a water container as a manometer. The water transported into another container indicates volume of permeated gas. The experiments were carried out at ambient temperature (27°C).

The ideal selectivity is based on gas permeation through the membrane. The selectivity for Gas A

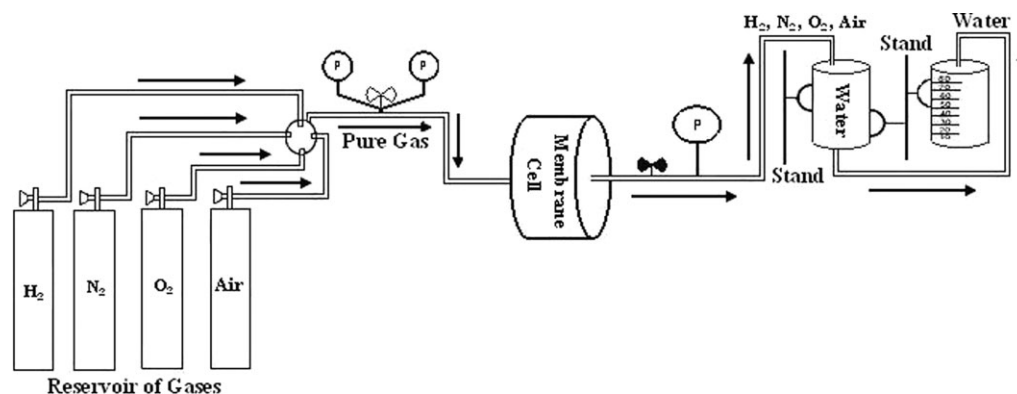


Figure 2 Apparatus for measurement of gas permeation.

relative to Gas B is characterized by the ideal separation factor α defined by,

$$\alpha = \frac{P_A}{P_B} = \frac{D_A}{D_B} \times \frac{S_A}{S_B}$$

where D is the diffusion coefficient of the gas in the polymer, S is the gas solubility and P_A is the permeability of Gas A, and P_B is the permeability of Gas B through the membrane.³³ The ratio D_A/D_B can be viewed as mobility selectivity and the ratio S_A/S_B as solubility selectivity. The selectivity is a measure for the difference in permeabilities (the relative ease with which species can permeate) of different components. In other words, it is a measure for the membrane separation effectiveness.

Scanning electron microscopy

The crosssections of the prepared membranes were observed using scanning electron microscopy (SEM) (XL30, Philips, The Netherlands). The membranes were frozen in liquid nitrogen and broken. They were transferred into the microscope with a sample holder after sputtering with gold as the conductive material. The SEM studies were carried out at room temperature and 25 kV.

Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) spectra were measured in absorbance mode on a Perkin-Elmer FTIR spectrometer with a temperature control cell. The spectra were measured in the range of wave numbers 500–2000 cm^{-1} . All the spectra were measured at a resolution of 4 cm^{-1} .

RESULTS AND DISCUSSION

Effect of PWA on membrane morphology

The morphologies of the membranes prepared from PVA/PWA/water are illustrated in Figure 3. The

10 wt % PVA membrane demonstrates a dense structure. The flat membranes obtained with various concentrations of PWA show a relatively porous structure.

Dense structure for PVA membrane is due to the fast exchange rate between solvent–polymer during the evaporation of solvent. Addition of PWA particles in the casting solution causes a delay time in exchange rate between solvent and polymer in phase inversion stage. By increasing the concentration of PWA to 6 wt %, porous structure appeared instead of dense configuration. This is due to a slow exchange rate of the solvent and polymer, resulting from an increase in the viscosity of the polymer solution. Moreover, the molecular interaction between $\text{C}-\text{OH}_2^+$ groups of PVA and $[\text{PW}_{12}\text{O}_{40}]^{3-}$ of PWA is feasible³⁴ due to the intermolecular hydrogen bonding between hydroxyl groups of PVA and PWA.²⁶ Higher degree of interaction leads to more rigid and compact polymer structure.²⁶

Effect of PWA on membrane performance

The performances of the PVA membranes are depicted in Figure 4. For N_2 , O_2 and air, the fluxes were improved from 50,000 to around 160,000, 140,000, and 80,000 $\text{L m}^{-2} \text{h}^{-1}$, respectively. For H_2 , this was enhanced from 110,000 to 230,000 $\text{L m}^{-2} \text{h}^{-1}$. Flux improvement is attributed to the increase in membrane porosity. The prepared membrane from PVA without PWA obtains a compact structure with low permeation of gases through the membrane. Addition of PWA results in higher porosity and greater permeation of gases. This is improved by further addition of PWA.

Permeability enhancement for N_2 is higher than O_2 . This may be due to the interaction between O_2 molecules with oxygen atoms in PWA structure. The permeation of air (20% O_2 and 79% N_2) is higher than O_2 and lower than N_2 . High permeability of H_2 is due to the small size. Moreover, the POM membranes allow selective permeation of protons.³⁵

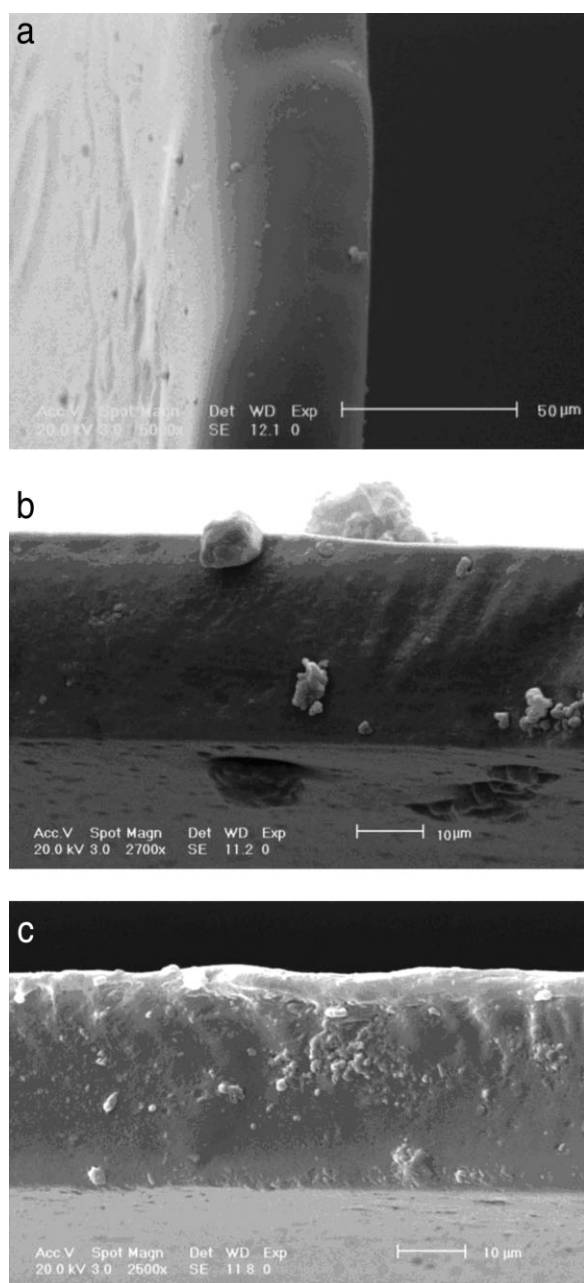


Figure 3 SEM micrographs of crosssection of 10 wt % polyvinyl alcohol membrane with and without various percentages of PWA: (a) 0 wt %, (b) 2 wt %, and (c) 6 wt %.

The ideal selectivity of gas pairs with various concentrations (0–6 wt %) of PWA are reported in Figure 4(b). By increasing the concentration of PWA to 6 wt %, the selectivity of the membrane was slightly improved for N_2 /air (from 1 to 1.2). For N_2 / O_2 pair, the initial drop (from 2.5 to 1.5) was followed by a slight increase (1.5–1.9). Moreover, the selectivity was decreased for H_2 /air (from 2.8 to 1.8) and H_2 / N_2 (from 2.2 to 1.7) by increasing the PWA concentration.

Addition of PWA in the casting solution enhances the selectivity for H_2 / O_2 from 2 to 2.8. The ideal

selectivity is a function of the permeability of gases, which depends on the concentration of PWA. The presence of PWA enhances the permeation of H_2 more rapidly compared with O_2 . This results in higher selectivity for H_2 / O_2 pair.

Fourier transform infrared spectroscopy

The FTIR spectra of PVA/PWA membranes were measured in the range of 500–2000 cm^{-1} for structural elucidation. The primary structures of supported HPAs were identified by comparing their FTIR absorbance bands to those of bulk HPAs. This arrangement gives rise to four types of oxygen bands between 1200 and 700 cm^{-1} , a fingerprint region for these compounds. Bulk PWA shows the characteristic of IR bands, 1080 (P–O in central tetrahedral), 985 (terminal W=O), 890, and 814 (W–O–W) associated with the asymmetric

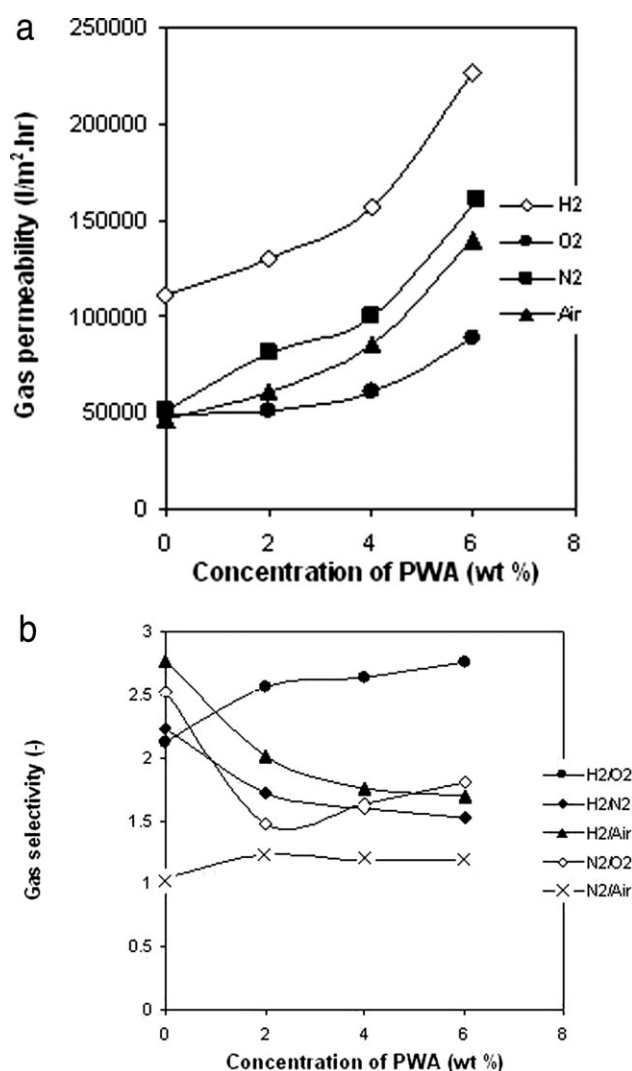


Figure 4 Effect of PWA concentration on permeability and selectivity of gases: hydrogen, oxygen, nitrogen, and air at 40 °C.

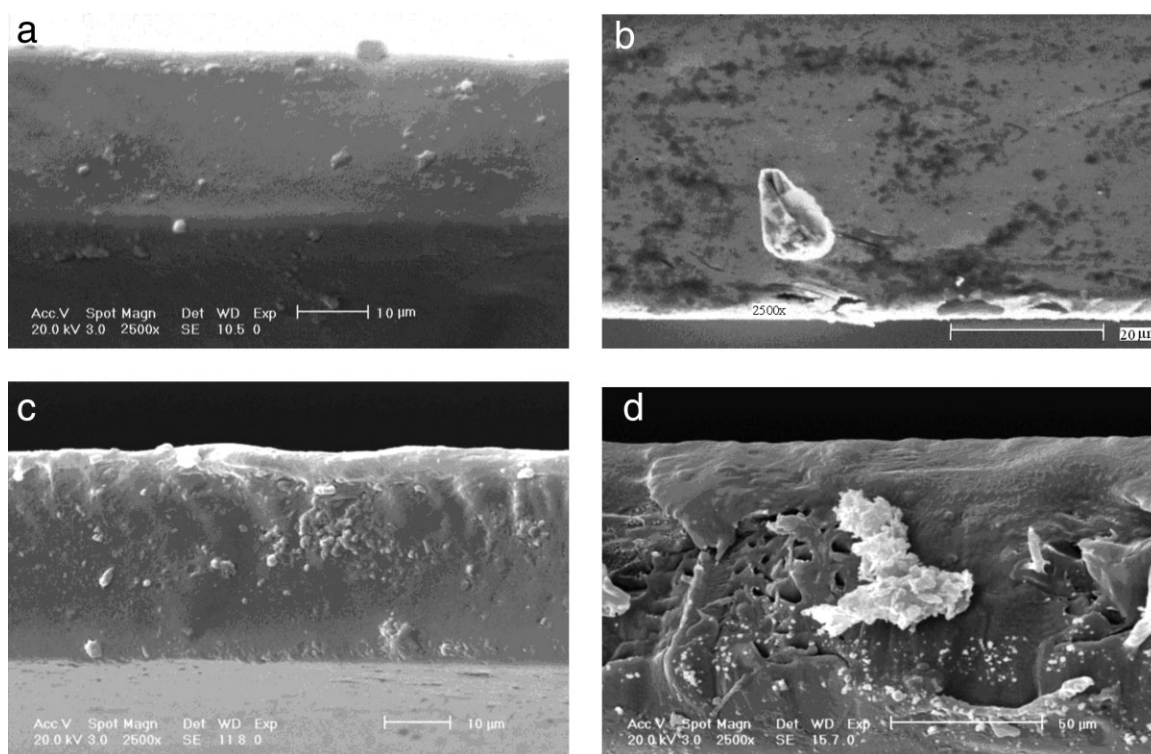


Figure 5 SEM micrographs of membrane crosssections prepared from 10 wt % PVA and 6 wt % PWA at: (a) 10°C, (b) 27°C, (c) 40°C, and (d) 80°C.

vibrations in the Keggin polyanions. All peaks of HPA are observable without any change compared with the bands of pure PWA. However, the shapes of bands are changed. Characteristic bands of PWA were overlapped with bands of PVA. This is the main reason for alteration of the shape. In summary, Fourier transform infrared spectra indicate that significant amount of PWA was maintained in the polymer matrix even after several hours of immersion in water.

Effect of solvent evaporation on morphology and performance of polyvinyl alcohol membrane

Flat-sheet membranes were prepared by dry-phase inversion at different temperatures (10, 27, 40, and 80°C) with constant concentration of PVA (10 wt %) and PWA (6 wt %). As expected, no deterioration was observed in membranes due to high temperature. The temperature in phase inversion stage affects the membrane morphology. This is followed by alteration of membrane performance.

Effect of solvent evaporation temperature on membrane morphology

Morphologies of the membranes prepared from ternary systems of (PVA/PWA/H₂O) with 10 wt % PVA and 6 wt % PWA at different temperatures are shown in Figure 5. Compact and porous structures

were obtained for the membrane prepared at 10 and 27°C. A comparison between the membranes prepared at 40 and 80°C implies that the number and size of voids are improved with increasing the temperature in the phase inversion stage. This is due to the effects of temperature on exchange rate between solvent and polymer. Evaporation of solvent from casting solution at elevated temperature results in complete and fast withdrawal of solvent from casting solution. In summary, temperature improvement during solvent evaporation results in formation of porous membranes.

Effect of solvent evaporation temperature on membrane performance

The effect of coagulation temperatures (10, 27, 40, and 80°C) on membrane performance is depicted in Figure 6. The membrane with 10 wt % PVA and 6 wt % PWA was studied in this section. For membrane with solvent evaporation at 10°C, the permeation of gases was low (around 100,000 L m⁻² h⁻¹). This was improved to 150,000 for oxygen, 250,000 for air, 380,000 for nitrogen, and 600,000 L m⁻² h⁻¹ for hydrogen by increasing the temperature up to 80°C. The general observation indicates that enhancing the temperature of solvent evaporation, leads to the increment in gas permeation. This may be attributed to the improvement in the membrane porosity with increasing the temperature during solvent

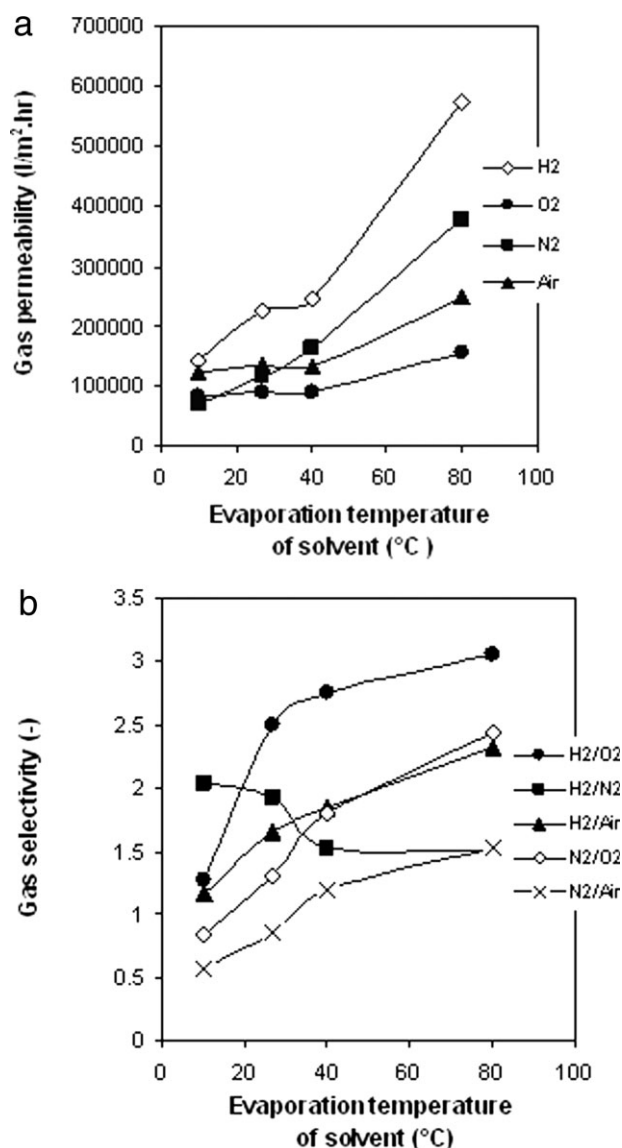


Figure 6 Effect of solvent evaporation temperature of membranes prepared with 10 wt % PVA and 6 wt % PVA on flux (a) and ideal selectivity (b) of hydrogen, oxygen, nitrogen, and air.

evaporation. This enhancement was low for O₂ compared with the other gases. This is due to the interactions between PWA particles and O₂ molecules.

The ideal selectivity for PVA membranes prepared at different temperatures is reported in Figure 6(b). For hydrogen/oxygen pair, by increasing the temperature from 10 to 80°C, the selectivity was improved from 1.3 to 3.2. The presence of PWA in the casting solution results in lower flux for O₂ and higher flux for H₂. The ideal selectivity is based on gas permeation through the membrane. A slight decrease (from 2.0 to 1.5) was obtained for H₂/N₂ selectivity with increasing temperature in the phase inversion stage. This may be due to increment in the permeation of gases (H₂ and N₂) with increasing the temperature of solvent evaporation. Furthermore, the selectivity

of PVA membrane was increased for N₂/O₂ (from 0.8 to 2.5), H₂/air (from 1.2 to 2.4), and N₂/air (from 0.6 to 1.5) with increasing the temperature from 10 to 80°C. Increasing the temperature of coagulation process enhances the permeation of some gases (H₂ and N₂) more than the permeation of others (O₂ and air). In summary, membrane performance was strongly dependent on the solvent evaporation temperature in the phase inversion stage.

CONCLUSIONS

Addition of PVA in the casting solution exhibited a great influence on membrane morphology and performance. This is via an increment in the number of voids in the membrane structure. HPA acts as a water-soluble pore-forming additive leading to the formation of membranes with higher permeation for some gases. The PVA particles allow higher permeation for H₂ and N₂ compared with O₂ molecules. This results in higher selectivity for H₂/O₂ pair. Increasing the evaporation temperature during phase inversion leads to membrane with higher porosity and greater flux. The proposed changes in the structure resulted in a membrane with improved performance e.g. higher selectivity for H₂/O₂. This separation is of utmost importance in practical applications.

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