Preparation and characterization of an asymmetric porous poly(vinyl chloride)/poly(methyl methacrylate-co-methacrylic acid) membrane

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ABSTRACT: Poly(vinyl chloride) (PVC) based membranes were prepared via a phase inversion method by casting a mixture solution containing PVC, poly(methyl methacrylate-co-methacrylic acid) (P(MMA-MAA)), and N-methyl pyrrolidone, using water as a coagulant. Measurement of the glass transition temperature showed that a PVC/P(MMA-MAA) system is virtually miscible. Cross-sections of the membranes showed that they were asymmetrical and had finger-like structures. Addition of P(MMA-MAA) to the PVC casting solution resulted in larger pores on the membrane surface, and the porosity and size of the finger-like pores increased as the content of P(MMA-MAA) increased. It was found that adding P(MMA-MAA) increased the porosity of the PVC membrane resulting in a higher permeation flux and hydrophilicity and lower rejection of bovine serum albumin, but a lower tensile strength and elongation at break.

KEYWORDS: N-methyl pyrrolidone, polymer blends, hydrophilicity, phase inversion, finger-like structure

INTRODUCTION

Phase inversion is the most commonly employed commercially available method for preparing microporous polymeric membranes[1,2]. In this method, a homogeneous polymer solution is cast on a suitable support and immersed in a coagulation bath containing a nonsolvent which is usually water. The exchange of solvent and non-solvent induces separation of the system into polymer-lean and polymer-rich phases. The polymer-lean phase disperses into a concentrated polymer-rich phase and responds to the formation of a porous structure. The polymer-rich phase solidifies after phase separation, and forms the membrane[3]. Many thermostable and chemical-resistant polymers such as poly(vinylidene fluoride), polysulphone, poly(ether imide), polyacrylonitrile, and cellulose acetate can be used to make microporous membranes using this method[4]. However, these materials are expensive.

Poly(vinyl chloride) (PVC), a polymer with outstanding properties, is used to fabricate microporous membranes due to its stiffness, excellent resistance to abrasion, acids, alkaline and microbial corrosion, and particularly low cost. Some studies have focused on the preparation of flat PVC ultrafiltration and microfiltration membranes using phase inversion[5–8]. A promising PVC ultrafiltration and microfiltration membrane for water treatment has been prepared[9].

However, the hydrophobicity of PVC causes heavy fouling on the membrane surface when a solution containing protein-like substances is treated.

Blends of polymers are easy to prepare using phase inversion. The addition of a second polymer to the casting solution brings about modification of the membrane structure[10]. In recent years, many studies reported using the phase separation technique to blend other polymers with PVC to improve its water flux and hydrophilicity. Some hydrophilic polymers blended with PVC, such as poly(methyl methacrylate)[11], poly(acrylonitril-co-methyl methacrylate)[12], polyacrylonitrile[13–15], poly(vinyl butyral)[16], carboxylated poly(vinyl chloride)[17], poly(ethylene glycol) and poly(vinyl pyrrolidone)[18] were studied. However, the main problem in blending is that most polymer pairs are rather immiscible.

In this work, poly(methyl methacrylate-co-methyl acrylic acid), or P(MMA-MAA), which will henceforth be abbreviated to PM, was selected to blend with the PVC dope solution. It was expected that PM would improve the hydrophilicity of PVC membranes because the monomer contains a carbonyl (C=O) and carboxylic (COOH) group. Moreover, a weak hydrogen bond responsible for the miscibility could be formed between PVC and PM[17]. This work aimed to prepare asymmetric membranes from a ternary solution of PVC, PM, and N-methyl pyrrolidone (NMP)

by the phase inversion method. The effect of PM concentration on the hydrophilicity, morphology, and transport properties of the membranes will be discussed.

MATERIALS AND METHODS

Blend solution and membrane preparation

The PVC used was a commercial product of TPC Paste Resin Co. (Thailand). The degree of polymerization was 1470. PM and anhydrous NMP were purchased from Aldrich. NMP was used as a solvent without any further purification.

The blend solutions based on PVC and PM were prepared by dissolving the two polymers in NMP at 60–65 °C in various ratios (Table 1). The transparent homogeneous solutions obtained were used within a week.

The cloud points of the casting solutions were obtained by measuring the amount of distilled water that needed to be added to the casting solution to make it turbid and not redissolve within 24 h. The viscosity of the diluted casting solutions (0.4 wt%) were measured using an Ubbelohde capillary viscometer at 30 ± 1 °C.

Each membrane was prepared using the classical phase inversion method with water as the coagulant. PVC/PM blend solutions were cast on a glass plate with a casting rod. The thickness of the cast films was fixed at 250 μm. The films were pre-evaporated for 30–90 s in air (25 °C, RH $65 \pm 5\%$) and then immersed in a 25 °C water bath for complete precipitation. The membranes were removed from the glass plate, washed thoroughly in a large amount of distilled water, and then stored in distilled water until use.

Determination of membrane properties

To characterize the compatibility of PVC and PM polymers, the glass transition temperature (T_g) of the blend was measured using a differential scanning calorimeter (Perkin Elmer, DSC7). The sample en-
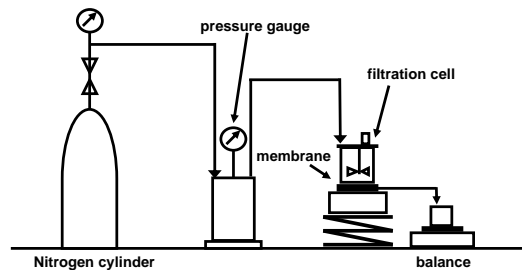
Fig. 1 Schematic diagram of a dead-end stirred cell filtration system.

capsulated in an aluminium pan was heated from 30 to 200 °C at a rate of 10 °C/min in a nitrogen atmosphere.

Specimens were prepared by cutting the casting film into pieces. The surface of the film was then examined using a Fourier transform infrared spectrometer (FT-IR) with attenuated total reflection mode (ATR-IR: Equinox 55, Bruker). To measure the contact angle, a water droplet of a constant volume was placed on the membrane surface by using an automatic interfacial tensiometer (Kyowa Inc). The angle was measured 17 ms after the water droplet made contact with the membrane. All measurements were made in air (25 °C, RH $55 \pm 5\%$).

The cross-sectional morphology of the membranes obtained was characterized by SEM (JSM 5200). The membranes were cut into pieces of various sizes, immersed in liquid nitrogen for 30–60 s, and then broken. The fractured membranes were coated with gold before analysis.

The tensile strength and elongation at break of the membranes were measured using a universal testing machine (Lloyd). The measurements were carried out at room temperature and at a pull rate of 5 mm/min.

To measure the transport and separation properties of the membranes, the ultra filtration experiments were carried out using a laboratory-scale system (Fig. 1) at room temperature using an operating pressure of 0.1 MPa. The pure water flux J was obtained from

$$J = \frac{Q}{A\Delta t}$$

where Q is the quantity of permeate collected, Δt is the sampling time, and A is the membrane area.

The solute rejection of the blend membranes was tested with 0.1 g/dl of bovine serum albumin (BSA) with an average molecular weight of 67 kDa (Fluka). The protein concentration was measured by spectrophotometry (UV-model Lambda 25, Perkin Elmer) at a wavelength of 280 nm. The solute rejection, R, of

Table 1 Composition, water content at cloud point, and relative viscosity (ν) of PVC/PM/NMP casting solutions.

PVC (wt%)	PM (wt%)	NMP (wt%)	Water content at cloud point (wt%)	ν^a
14	0	86	6.85	1.58
13	1	86	6.33	1.48
12	2	86	6.34	1.47
11	3	86	6.72	1.43
8	6	86	6.27	1.41

[a] measured in NMP at 30 ± 1 °C at a total concentration of 0.4 g/dl

BSA was calculated using

$$R = \left(1 - \frac{C_{\mathrm{p}}}{C_{\mathrm{f}}}\right) \times 100\%$$

where C_{p} and C_{f} are the protein concentrations in the permeate and feed, respectively.

RESULTS AND DISCUSSION

Thermodynamics of membrane-forming system

In order to understand the membrane-forming system, the cloud points and viscosity of the casting solution system should be investigated. The cloud point indicates that a small amount of water is needed to induce demixing for all compositions. No significant difference of the cloud point was observed when PM was added to the casting solution (Table 1). However, the relative viscosity decreased with increasing PM. Membranes obtained from a pure PVC casting solution possess the highest relative viscosity which hinders the exchange between water and NMP during phase separation. Under this condition, membranes can be expected to have low porosity and permeability.

Miscibility of PVC/PM blended membrane

Generally, the compatibility of blend polymers is an essential requirement for efficient use of blends. It is well known that the T_{g} characterizes the segmental motion of polymers. The observation of T_{g} in the polymer blend is usually taken as proof of miscibility of the polymer mixtures. For an immiscible multi-phase system, the T_{g} of each phase can be identified, and takes the values for each homopolymer. A single glass transition temperature can be obtained if the system is completely miscible[17]. A plot of heat flow versus temperature (Fig. 2) indicates that the PVC/PM blend has single T_{g} value up to the highest concentration of PM employed. Hence it can be concluded that the PVC/PM system was completely miscible.

Surface characterization

It was expected that the hydrophilicity of the blend membrane surface would be improved by the addition of PM in the PVC solution. In order to verify the existence of PM on the film surface, the surface characterization of blend membranes was then performed by FT-IR with ATR-IR. FT-IR spectra (Fig. 3) of blend membranes showed C=O (1730 cm^{-1}) and C–O (1191 and 1151 cm^{-1}) functional group bands. These were attributed to the addition of PM.

The improvement in the surface properties of membrane was also confirmed by measuring the contact angle of distilled water on the membrane surface
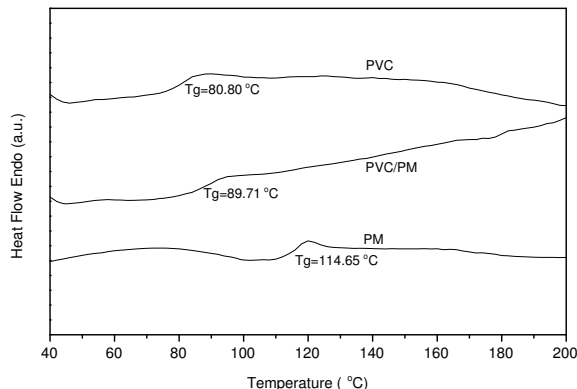

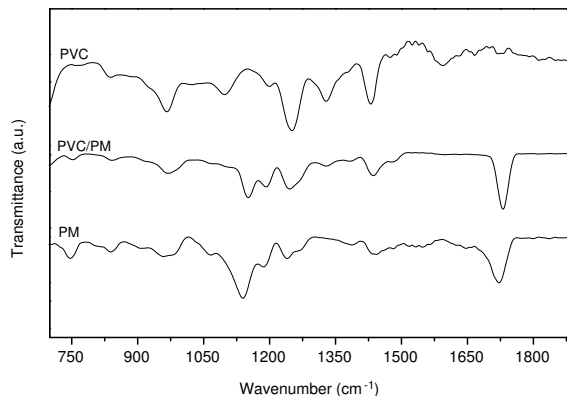**Fig. 2** Differential scanning calorimeter thermograms of PVC, PVC/PM blend, and PM.

Fig. 3 FT-IR spectra of PVC, PVC/PM blend membrane, and PM.

(Fig. 4). The PVC membrane had the highest contact angle of 80°, indicating the lowest hydrophilicity. The decreasing water contact angles of the blend membranes with increasing the PM content meant that the introduction of PM could effectively hydrophilize the PVC membrane.
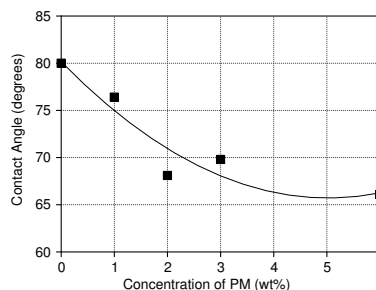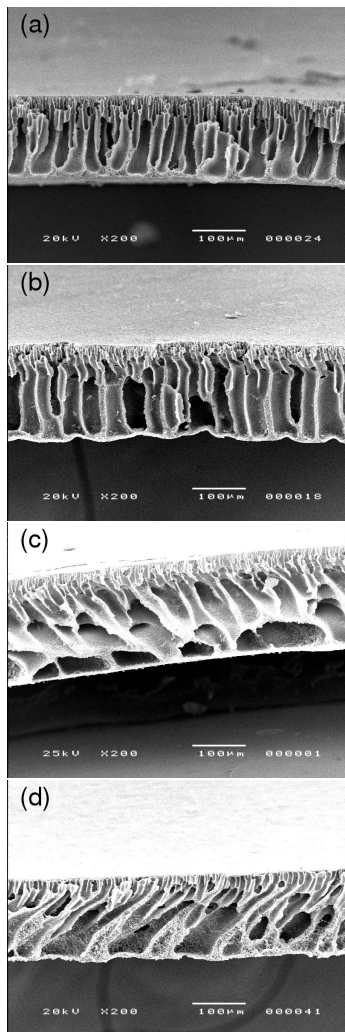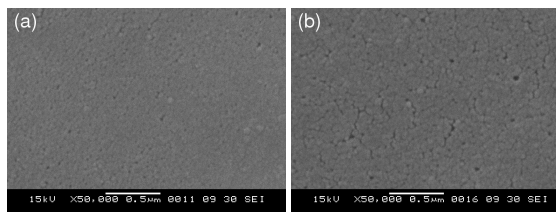

Fig. 4 Water contact angle of PVC/PM membrane as a function of the PM concentration of the casting solution.

Morphology

The SEM images of cross-sections of PVC and PVC/PM blend membranes (Fig. 5) show that the PVC pure and PVC blend membrane have an asymmetrical structure consisting of two skin layers (a top and bottom skin layer) and a finger-like support layer or macrovoid. Generally, this structure is obtained when the casting solution is immersed directly into a non-solvent bath[19]. As the PM content increases, the skin layer become thinner and the finger-like pores become larger and change in shape. The membranes from the casting solution of pure PVC and 2 wt% of PM have straight finger-like pores with a lower volume and thicker walls than the inclined finger-like

Fig. 6 SEM photographs of surface of membranes. Casting solution PM concentrations: (a) 0 wt% (b) 6 wt%.
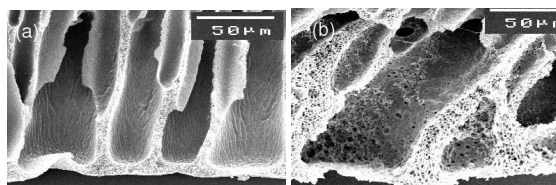
Fig. 7 SEM photographs of walls of membranes. Casting solution PM concentrations: (a) 0 wt% (b) 6 wt%.
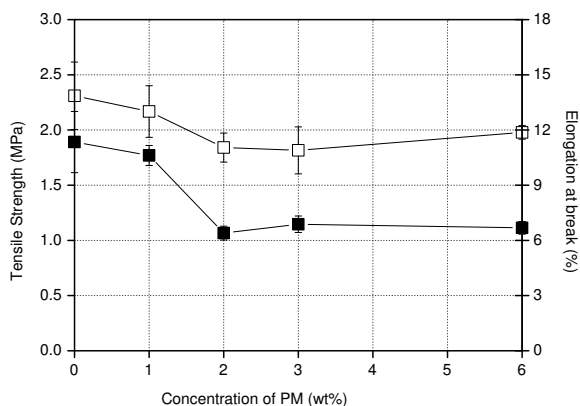
pores obtained from the casting solution with 3 and 6 wt% of PM.

The surfaces of pure PVC and PVC/PM membranes are shown in Fig. 6. Many large pores are visible on the surface of the 6 wt% PM blend membrane. The walls of the finger-like structures in the 6 wt% PM membrane (Fig. 7) also have more pores and exhibit a more sponge-like structure than in the case of pure PVC. A similar finding was reported when poly(methyl methacrylate) was present in a poly(vinylidene fluoride) doping solution[20]. Moreover, Rameh and Galkar[17] found a similar result for PVC/carboxylated poly(vinyl chloride) blend membranes. They thought that the high porosity might result from repulsive forces between carboxylic acid groups of the polymer added to the dope solution.

Mechanical and transport properties

The tensile strengths and the elongations at break of blend membranes were lower than for pure PVC (Fig. 8). This phenomenon can be attributed to the membrane structure. A cross-section with larger macrovoids, more porous walls, and thinner skin layers results in a reduction in the strength of the membrane.

The addition of PM to PVC greatly improves the water flux and lowers the rejection of BSA (Fig. 9). This is a result of the larger volume and more porous walls of the finger-like pores in the PVC/PM membrane compared with the pure PVC membrane.

Fig. 5 SEM photographs of membranes. Concentrations of PM in casting solutions: (a) 0 wt% (b) 2 wt% (c) 3 wt% (d) 6 wt%.

Fig. 8 Tensile strength (□) and elongation at break (■) of PVC/PM blend membranes as a function of casting solution PM concentration.
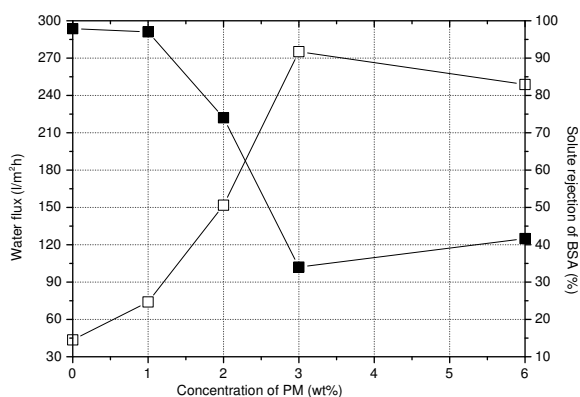
Fig. 9 Pure water flux (□) and solute rejection of BSA (■) of PVC/PM blend membranes as a function of the casting solution PM concentration.

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