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A Novel High-Flux Asymmetric p (VDF-HFP) Membrane with a Dense Skin for Ethanol Pervaporation

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The asymmetric p (VDF-HFP) pervaporation membrane with an ultra-thin dense skin layer was fabricated through the controlled solvent evaporation method and the two step-coagulation bath-phase-inversion method. The membrane was used to concentrate ethanol from an aqueous solution. The total flux reached 2.4 kg·m^{-2}·h^{-1}. Ethanol was concentrated from 5.1 wt. % to 24.0 wt. %.

The separation of ethanol/water mixture is very important for the production of ethanol from biomass [1]. Especially in the lignocellulosic ethanol fermentation broth, the final bioethanol concentration is 3.0 ~ 5.0 wt. % due to the presence of impurities and fermentation inhibitors [2]. The organoselective pervaporation (PV) process is one of the most promising processes in ethanol extraction and concentration because it is an energy saving and environmental friendly process. And the PV process is easy to couple with ethanol fermentation [3]. The performance of the process is primarily determined by the membrane materials. For decades, Si-based materials such as polydimethyl-siloxane (PDMS), poly (trimethylsilylpropyne) (PTMSP) have become objects of interest because of their predominant selectivity [4~8]. However, their selectivities are limited due to the poor resistance to swelling. And the flux is very low because the prevalent preparation method produces a very thick dense layer. Industrial application calls for membranes with higher efficiency, which means much higher permeation rates and reasonable separation factors. The PV efficiency is determined by dissolving, diffusion and desorption processes, which are determined by the material and the structure of the membrane. Therefore, membrane fabricated of ethanol selective material and with a structure that facilitates diffusion, can extract ethanol from water efficiently. This work aimed at finding a new material and fabricating a membrane with an asymmetrical structure, which is a much thinner dense skin than the PDMS PV membrane and a strong inner support.

Theoretically, F-based materials, such as poly (vinylidene fluoride) (PVDF) and polytetrafluoro ethylene (PTFE), are supposed to be the ideal materials for ethanol separation from water because these materials are more hydrophobic than PDMS. However, because of lack of a suitable solvent, PTFE can only be fabricated as porous membrane. PVDF membrane with a dense layer has a low selectivity and permeation rate because of the compact semi-crystal polymer structure. The F-based materials are commonly used as graft materials onto PDMS in current research. Researchers used F-based polymers like styrene–fluoroalkyl acrylate graft copolymers to modify PDMS membrane had achieved remarkable separation factors but poor flux [9].

Compared with PVDF, poly (vinylidene fluoride-co-hexafluoro -propylene), p (VDF-HFP) possesses lower crystallinity and higher free volume due to the incorporation of an amorphous phase of hexafluropropylene (HFP) into the main constituent vinylidene fluoride (VDF) blocks. Addition of the HFP group also increases the fluorine content and makes p (VDF-HFP) more hydrophobic than PVDF [10]. However, the PV performance of the homogenous p (VDF-HFP) membrane was not impressive because its structure was too dense to permeate any molecules under regular conditions. This paper aims at fabricating a new p (VDF-HFP) membrane with a super thin dense skin, which allows ethanol to diffuse through the membrane with very high flux.

The first commercial reverse osmosis (RO) membrane was fabricated in 1960, and it was based on the L-S method, devised by Loeb and Sourirajan [11]. They introduced phase inversion technology to produce an asymmetrical membrane with one ultrathin and relatively dense skin layer with very high flux. When the casting membrane was submerged into a coagulation bath, a polymer on the surface accumulated quickly, forming a relatively dense layer. The non-solvent inward diffusion rate decreased because the dense layer blocked it; the speed of polymer accumulation decreased. This way, under the dense skin, a porous layer formed. However, L-S method was often used to fabricate micro filtration (MF), ultra filtration (UF) or RO membranes which all have pores on the surface. But the dense skin is necessary for any PV process. In phase inversion process, the solvent outward diffusion rate and the non-solvent inward diffusion rate significantly influence the asymmetrical structure of the membrane. So, with an appropriate coagulant, additives and casting conditions, it is possible to fabricate an asymmetrical membrane with a dense layer and a porous principal part which can balance permeation rate and separation factors. Based on this we assume that, exposing the membrane to the air in a controlled temperature and humidity for a specified time, the solvent on the surface will evaporate before phase separation starts. So the polymer on the surface will form a gelatinous layer and then a dense skin after immersing it into the specific coagulation baths. In this work, p (VDF-HFP) is for the first time, fabricated as an asymmetrical PV membrane through the controlled solvent evaporation method combine the two step-coagulation-bath phase-inversion method.

P (VDF-HFP) polymer (Aldrich, USA. Mw, 400,000; Mn, 130,000; polydispersity index, PDI, 1.77) was dried in a vacuum oven at 120 °C for 2 days. 1.0 ~ 5.0 g LiCl was dissolved in 100 g N, N- dimethylacetamide (DMAc) to form a clear solution, and then blended with 15 g p (VDF-HFP) at 100 °C to form a homogeneous casting dope. The solution was degassed and kept in an oven at 80 °C.

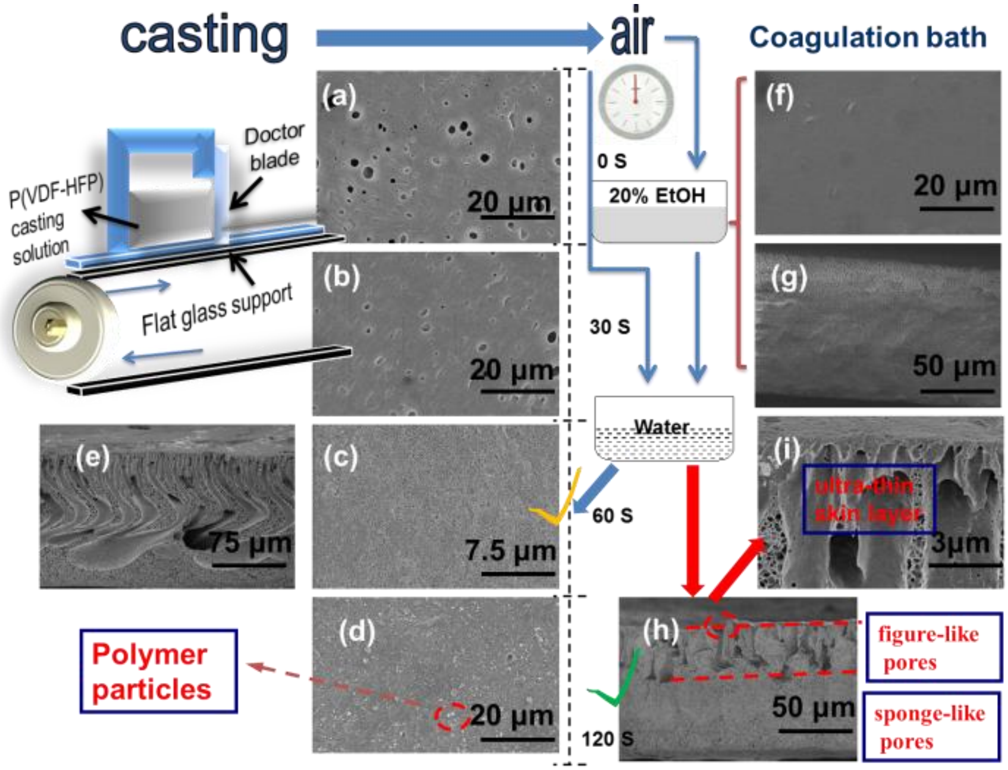

Fig. 1 SEM images of membranes: (a) using water as coagulation bath, exposure time 0 s; (b) using water as coagulation bath, exposure time 30 s; (c) using water as coagulation bath, exposure time 60 s and (e) its cross-section view ; (d) using water as coagulation bath, exposure time 120 s; (f) using 20% EtOH aqueous solution as coagulation bath, exposure time 60 s and (g) its cross-section view; (h) cross-section view of first using 20% EtOH aqueous solution then using water as coagulation bath, exposure time 60 s and (i) its magnified view.

The casting dope was evenly spread on a glass plate. Then the spread dope is exposed in the air for 0~120 s at a control temperature and pressure. In this work, the relative humidity of the air was carefully controlled to be less than 50%; the casting temperature is 20 °C. The glass plate was then immersed in the mix coagulation bath at 20 °C for 60 s to form a nascent state membrane. The mix coagulation is ethanol aqueous solution with ethanol concentration ranging from 0% to 25%. The membrane was then submerged into pure water at 50 °C to form the final membrane. To protect the micro voids within the membrane, the final membrane was submerged to ethanol, then into an n-hexane coagulation bath to thoroughly exchange water and additions [12]. After the precipitation was completed, the membranes were removed and dried at 50 °C.

The effect of LiCl is to increase the effective porosity without changing the pore size of the membrane, thus greatly enhancing the overall flux through the membrane. But when the addition of LiCl overdoses, the membrane would be fragile and unstable. In this work, the ratio of LiCl to DMAc is 3.0 g to 100.0 g.

Scanning electron microscopy (SEM) photomicrographs (Hitachi, S-4800) and PV experiments were performed according to Qu's work [13]. Permeate flux, J, was calculated using the equation: J ($g\ m^{-2}\ h^{-1}$) = Q/AT, where Q (g) was the total amount of permeate that passed through the membrane during an experimental time interval T (h) at a steady state, and A (m^2) was the effective area of the membrane. The separation factor was determined as $\alpha_{e/w} = (Y_e/Y_w)/(X_e/X_w)$ where X_e, X_w, Y_e and Y_w denote the mass fraction of components e (ethanol) and w (water) in the feed and the permeate side, respectively. The degree of swelling (DS) of the membrane at a given interval is defined by following equation: $DS = (m_t - m_0)/m_0 \times 100\%$, where m_0 and m_t are the weights of dry and solvent swollen membranes, respectively. The swelling experiments were performed at a constant temperature of 45 °C, the same temperature at which the PV experiment was performed. The membranes were weighed at room temperature by using an analyzing balance. The free liquid on the surface of the swollen membrane was removed carefully and quickly using filter paper before weighing. The PV performances of all the dense membranes were tested. Each membrane was fabricated under a different condition and tested for 5 times. The reproducibility was calculated based on the PV performance.

To form a membrane with a dense surface, we exposed the spread casting dope in the air for 0-120 s in order to make the solvent on the surface evaporates before the phase separation started. It is reported that when the relative humidity of the air reached 65%-100% the phase inversion will happen [14]. In this work, the relative humidity of the air was carefully controlled to be less than 50%. In addition, the casting temperature was set at 20 °C to avoid excess water absorption, which would have occurred at higher temperature. Fig.1 shows SEM pictures of membranes fabricated under different conditions. As seen from Fig.1 a-d, the exposure time in air significantly changed the surface morphology of the membranes, and the changes occurred very fast, even in only 2 minutes. After the membranes were exposed in air for more than 60 s, as shown in Fig.1 c and f, the surface of the membranes were dense and there is no hole on the skin of the membranes. When the exposure time is less than 60 s,

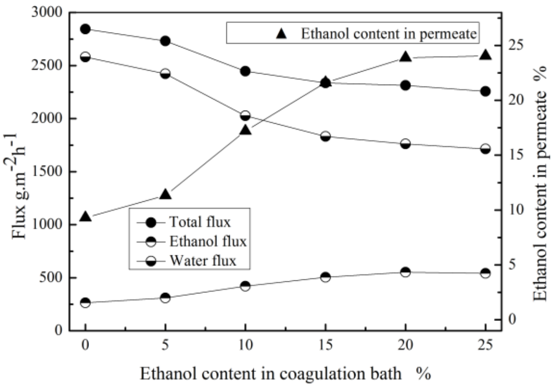

Fig. 2 Pervaporation performances of p (VDF-HFP) membranes at 40 ℃ for an aqueous solution of 5 wt % ethanol

Table1. Previous works about membrane pervaporation for ethanol separation from water

Membrane	Type	T (K)	Xe (wt.% feed)	Xe (wt% permeate)	Flux (g m^{-2} h^{-1})	Ref.
PDMS	Pure	313	2	15~17	110	15
	Cross linking	313	10	47	170	16
	Composite	313	5	32.9	1140	17
PTMSP	Pure	313	6	56	340	18
	Graft PDMS	303	7	70	61	19
PEBA	Silicalite	313	5	16	833	20
P(VDF-HFP)	Asymmetry	313	5.1	24.0	2428.0	This work

there are very obvious holes on the skin of the membrane. However, when the exposure time is more than 60 s, some particles were observed on the skin of the membrane. Because increasing the exposure time from 60 s to 120 s would have induced a problem of solvent over evaporation, which had caused the polymer to accumulate on the surface of the membranes. In Fig.1d, some small particles with a diameter of 0.1~0.2 μm were clearly observed. Thus, the exposure time was carefully optimized and controlled at 60 s. However, the surface of the membrane still appeared rough and porous. This is because the strong non-solvent made the exchange with solvent so severe that it was very difficult to form a smooth surface. Another undesirable result was that the interior of the membrane had many finger-like pores which made the membrane very fragile. A novel two-bath-step immersion phase inversion method was used in this work. The membrane was first submerged in the mixture of 20% ethanol at 20 ℃ to form a nascent membrane and then submerged in pure water at 50 ℃ to form the final membrane.

The morphology differences of using the various coagulation baths are compared in Fig. 1 f-i. The surface of the membrane submerged into water coagulation bath (c) is not as smooth as the membrane submerged into 20% ethanol aqueous solution coagulation bath (f). On the other hand, from the cross-section views we can see that the membrane only submerged in the 20% ethanol aqueous solution coagulation bath has sponge pores but no finger-like pores. Fig.1 h and i showed the membrane fabricated by the two-step-bath immersion phase inversion method. This membrane has a very thin dense skin and also has both finger-like pores and sponge pores within the membrane, which balances the PV performance and strength. The ethanol and water mixed solution is chosen as the first coagulation bath in order to control the exchange speed of solvent and non-solvent. Fig 1 shows that the 20% ethanol is crucial to forming the smooth surface. This is because 20% ethanol aqueous solution is a week non-solvent, its exchange speed with DMAc is relatively slow. On the other hand, the slow exchanging speed makes the p (VDF-HFP) accumulate evenly, which finally forms sponge structure. This produces a better mechanical structure, but a slower permeation rate. PV test shows the ethanol separation factor and total flux of the sponge-like membrane are 5.13 and 0.85 kg m^{-2} h^{-1}, respectively. Therefore, the second coagulation bath is applied before the membrane finally forms. Pure water is chosen as the strong non-solvent. The high exchange speed of water and DMAc leads to instantaneous polymer accumulation, forming finger like pores inside of the membrane. The temperature of the coagulation bath also has a strong effect on the membrane structure. In the first coagulation bath, we chose a 20% ethanol aqueous solution at 20 ℃ because phase inversion proceeded slower at the lower temperature, and produced the polymer gelation first. The second coagulation was 50 ℃ pure water. The reason that the higher temperature was applied here is because the kinetic of mass transfer increased as the temperature increased. And the accelerating of the mass transfer is very helpful to form the finger-like and interconnected sponge pores inside the membrane. The higher temperature also helped to rinse additions more quickly and thoroughly, which improved both the porosity and the PV performance. However, this improvement is limited because excessively high temperature leads to poor ethanol selectivity of the membrane.

The p (VDF-HFP) asymmetrical membrane was fixed into the PV module. And air pressure was maintained at 0.5 Mpa at the upstream side. During a 10h test, air pressure remained almost stable, showing that a dense membrane had been produced.

Fig. 2 shows that the flux and the ethanol concentration in the permeate side of PV through p (VDF-HFP) asymmetry membrane. When the ethanol concentration in the coagulation bath reached 20%, PV performance of the membrane reached the optimal point. The concentration of ethanol in the permeate side and total flux was 24.0% and 2428.1 g m^{-2} h^{-1} respectively.

The exposure time in the air after casting the dope onto glass and the composition of coagulation bath are proved to be the key roles to form the target structure. The surface of the membrane was shown to be dense when it was magnified 20,000 times. Our previous hypothesis that appropriate phase-inversion conditions can help to form the dense layer, is proven to be true. The asymmetrical structure was presented clearly in the cross-section view. The thickness of the dense layer was extremely thin while the rest part of the membrane was a porous, sponge-like structure. And most of the pores were interconnected making the penetration much more efficiently.

The permeation rate of the asymmetrical p (VDF-HFP) membrane is remarkably higher than the dominant PDMS material. That is mainly because the thickness of the dense skin of the p (VDF-HFP) membrane is ranging from 0.1~1.0 μm through optimizing conditions of the polymer, coagulations and other parameters. And the separation factors are competitive to the pure PDMS membrane which can be further improved in future works. Thus, by comparing the PV results of the asymmetrical p (VDF-HFP) membrane with other ethanol selective membrane reported in the references 15~20, we conclude that p (VDF-HFP) is an ideal membrane material. Ethanol concentration in the feed side is fixed to be 5 wt % because ethanol concentration in fermentation broth is 5~8 wt %. The ethanol concentration in permeate achieved 24.0 wt%, which can be integrated directly with the distillation process, saving considerable energy. It is reported that the ethanol concentration from 3.0 wt. % to 20.0 wt. % is the most expensive phase in the distillation process.

We found that the equilibrium swelling degree of membranes in 100% ethanol and 5% ethanol are averaged 1.1 and 1.4 respectively. The PV experiment was performed for 30 days. And no obvious performance attenuation was observed. The optimized p (VDF-HFP) membrane showed minor swelling and excellent mechanical performance.

Reproducibility experiments showed that only the membranes exposed to air for 60s and then submerged into the optimized two-step coagulation bath are qualified for ethanol pervaporation, which implies they must have a dense surface. These membranes exhibit high flux in the ethanol/water mixture PV experiments. The average values of separation factor and total flux are (5.5~6.4) and (2396.6~2453.1) g m^{-2} h^{-1}, respectively. The relative standard deviation values of the separation factor and total flux are 5.6% and 1.2% respectively, which demonstrates the high reproducibility of the asymmetric p (VDF-HFP) membrane.

Notes and references

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