

Improvement of hydrophilicity of porous PVDF membranes with LiCl additives

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Abstract: Porous polyvinylidene fluoride (PVDF) membranes blended with LiCl are prepared through the phase inversion method to obtain a good support layer for air dehumidification. The hydrophilicity of the resulting membrane is evaluated by water contact angle measurements and vapor adsorption tests. The moisture permeation performance of the membrane is measured by permeation tests in terms of total mass transfer coefficients and moisture permeability rates. It is found that water contact angles and water vapor adsorption capacities increase with the increasing LiCl content in the casting solution. As the LiCl content increases, the total mass transfer coefficient increases slightly at a low LiCl content (below 2.5%) and then improves greatly at a high LiCl content (above 2.5%), whereas the moisture permeation rate increases. The results demonstrate that LiCl can remarkably improve the hydrophilicity of PVDF membranes, and then greatly enhance moisture permeation performance.

Key words: porous polyvinylidene fluoride membranes; LiCl; hydrophilicity; dehumidification

Membrane-based dehumidification has been widely used in a wide range of fields such as chemical, electronic, and precision machine industries because of its low capital and low energy consumption. Various polymer membranes including cellulose acetate, polyethersulfone, Nafion, and poly(amideimide) are investigated for the removal of water vapor^[1-4]. It is well accepted that a thin thickness of a dense membrane favors moisture permeation. Composite membranes comprised of a dense active layer and a porous support layer are widely applied to obtain high permeability. The thin active layer provides the permselectivity to the membranes while the porous substrate layer acts as a mechanical support. The diverse hydrophilic membranes have been investigated as an active layer of the composite membrane for dehumidification^[5-7]. However, the support layer has been rarely concerned, though it also has important influences on performance^[8-9].

As a support layer of the composite membrane for dehumidification, an appropriate hydrophilicity is also essential as well as good mechanical properties^[9]. The hydrophilic support layer makes it easy to coat the hydrophilic active layer on it and enhances the transfer of water vapor. Among vari-

ous materials, polyvinylidene fluoride (PVDF) is a popular material for preparing porous membranes due to its excellent mechanical properties, good thermal and chemical stability as well as low cost. However, the hydrophobicity of PVDF brings some problems to its application in dehumidification as a support layer: 1) It is difficult to form the hydrophilic layer on it; 2) The attachment between the active layer and the substrate is poor, resulting in less stability of the composite membrane in moist environments; 3) The transport of water vapor through porous membranes is slow, inducing a low moisture permeability of the composite membrane.

Various strategies have been applied to improve the surface hydrophilicity of PVDF membranes. Basically, these methods include blending them with hydrophilic additives, surface modification with grafting hydrophilic monomers, surface coating, etc.^[10-12]. By comparison, blending is a convenient and efficient strategy to enhance the hydrophilicity and to control the membrane structure. Although there are some reports on the modified hydrophilicity of PVDF micro-filtration/ultrafiltration membranes by the blending of PVDF with amphiphilic polymers^[13-15], the expensive cost and rigorous preparation conditions limit their large-scale applications. Hygroscopic LiCl is a good additive because of its low cost. Unfortunately, its effects on the hydrophilicity and the water vapor permeation performance of membranes have almost not been discussed before.

In this paper, hydrophilic porous PVDF membranes are prepared by the phase inversion method using cheap LiCl as a hydrophilic additive. The hydrophilicity and water vapor permeability of the modified membranes are characterized by water contact angle measurements, vapor adsorption tests and permeation tests. Moreover, the influence of the LiCl content on the hydrophilicity and moisture permeability of porous PVDF membranes are also examined in detail.

1 Experimental

1.1 Materials

PVDF ($M_w = 3 \times 10^5$) is supplied by Shanghai Xilai Fine Chemical Co., Ltd., China. PEG-6000, anhydrous LiCl and N, N-dimethyl formamide (DMF) are supplied by Shantou Guanghua Chemical Factory Co., Ltd., China. Tap water is used as a non-solvent in the coagulation bath.

1.2 Membrane preparation

Flat sheet PVDF porous membranes are prepared by the phase inversion method. Casting solutions are prepared by dissolving the required amount of PVDF, PEG-6000 and LiCl in DMF at 50 °C. The composition of the casting solu-

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tion to prepare different membranes is shown in Tab. 1. The solution is cooled down and placed stand-still for de-bubbling. The solution is coated on a clean glass plate. The thickness of the membrane is controlled by a gap between a casting knife and a glass plate. Then the solution films are immediately immersed in a coagulation bath of tap water. The formed membranes are peeled off and washed thoroughly with water subsequently to remove residual solvents. Then they are dried for 24 h at room temperature.

Tab. 1 Composition of PVDF casting solution %

Membranes	w(PVDF)	w(DMF)	w(PEG-6000)	w(LiCl)
M ₀	9.0	88.6	2.4	0
M ₁	9.0	88.1	2.4	0.5
M ₂	9.0	87.6	2.4	1.0
M ₃	9.0	87.1	2.4	1.5
M ₄	9.0	86.6	2.4	2.0
M ₅	9.0	86.1	2.4	2.5
M ₆	9.0	85.6	2.4	3.0

1.3 Membrane characterization

The hydrophilicity of membrane is evaluated by contact

angle measurements between membrane and water droplets using the contact angle analyzer(OCA20, Dataphysics, Germany) at room temperature. The water vapor sorption capacity is tested using the sorption analyzer (Hydrosorb-1000, Quantachrome, USA).

1.4 Moisture permeation measurement

Similar to the method reported in Ref. [7], moisture permeation performance through the prepared membranes is measured in the test rig as shown in Fig. 1 in terms of total mass transfer coefficients and vapor permeation rates.

As plotted in Fig. 1, two air streams, one dry and one humid, flow through a membrane exchanger to exchange moisture. For the dry stream, ambient air is dehumidified and then is drawn through the exchanger for moisture exchange. For the humid stream, it is driven directly from the ambient to the exchanger. The membrane is sandwiched by two stainless steel half shells. The two air streams pass through the exchanger in a counter flow arrangement. Equal air flow rates are kept for the two air streams. The total mass transfer coefficient $K(\text{m/s})$ is calculated by the following equation:

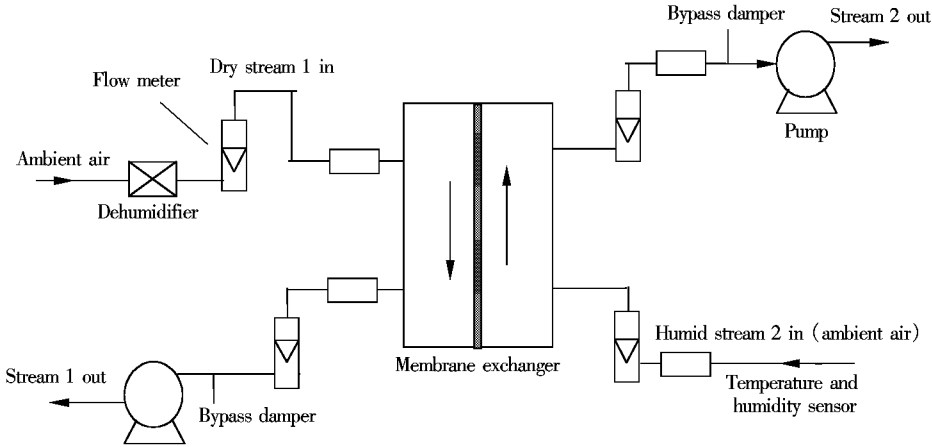


Fig. 1 Experimental set-up

$$K = \frac{\Delta W}{\rho_a A \Delta \omega_m} \quad (1)$$

$$P_c = \frac{\Delta W}{A} \quad (4)$$

where A is the transfer area of the membrane in the cell (m^2); ρ_a is the air density (kg/m^3); ΔW is the mass of vapor transferred through the membrane (kg/s); $\Delta \omega_m$ is the logarithmic mean humidity difference. ΔW is calculated as

$$\Delta W = \frac{V \rho_a}{3600} \frac{(\omega_{10} - \omega_{1i}) + (\omega_{2i} - \omega_{20})}{2} \quad (2)$$

where ω_{1i} and ω_{2i} represent the inlet humidities of air streams 1 and 2, respectively; ω_{10} and ω_{20} represent the outlet humidities of air streams 1 and 2, respectively; V is the air volume flow (m^3/h).

$\Delta \omega_m$ is calculated as

$$\Delta \omega_m = \frac{(\omega_{10} - \omega_{1i}) - (\omega_{2i} - \omega_{20})}{\ln((\omega_{10} - \omega_{1i})/(\omega_{2i} - \omega_{20}))} \quad (3)$$

And the vapor permeation rate $P_c (\text{kg}/(\text{m}^2 \cdot \text{s}))$ is calculated as

2 Results and Discussion

2.1 Hydrophilicity of membranes

The contact angle measurement is a convenient way to evaluate the relative hydrophilicity of membrane surfaces. The time dependence of contact angles between the water droplets and the surface of the membranes with different LiCl contents is shown in Fig. 2. As observed, the addition of LiCl in the casting solution decreases the initial contact angles of the membranes. Furthermore, the initial contact angles decrease from 94° to 62° with the increase in LiCl content. Meanwhile, the contact angle of a pure PVDF membrane almost remains unchanged within the measurement time, while the contact angles of membranes with different LiCl contents decrease gradually. Moreover, the decaying trend of the contact angle accelerates with the increasing LiCl content in the casting solution. The decrease in the initial contact angle and the increase in the decay rate can

demonstrate to a large degree that the addition of LiCl improves the hydrophilicity of the membranes. Similar analyses were also reported in Ref. [13].

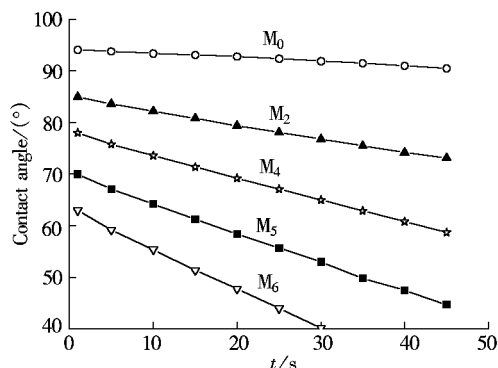


Fig. 2 Time dependence of contact angle of membranes

2.2 Vapor sorption tests

The adsorption and desorption isotherms of three membranes with different LiCl contents at 25 °C are presented in Fig. 3. The solid lines represent adsorption and the dashed lines represent desorption. It can be seen that the addition of LiCl in the casting solution greatly improves the moisture adsorption property of the membranes. For example, at 60% relative humidity, the moisture adsorption capacity increases by a factor of 5. 4. Moreover, PVDF membranes can adsorb more water vapor with a higher amount of LiCl in the casting solution. This result further indicates that hygroscopic LiCl enhances the hydrophilicity of the membranes.

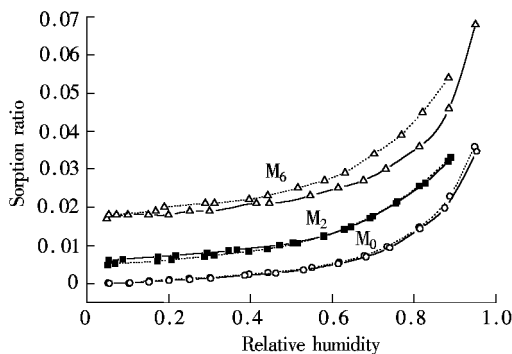


Fig. 3 Water vapor adsorption and desorption isotherms of membranes at 298 K

2.3 Moisture permeation performance

The moisture permeation performance of different membranes is measured by vapor permeation experiments in the test rig (see Fig. 1) in terms of the total mass transfer coefficient and the vapor permeation rate. The effects of LiCl content on the total mass transfer coefficient of PVDF membranes in different air flows are shown in Fig. 4. It can be seen that with the increase in LiCl content, K increases slightly at a low LiCl content (below 2.5%). As the LiCl content continues to increase, K increases greatly. As reported in Ref. [16], the total mass transport coefficient is defined as the inverse of moisture transport resistance in the exchanger. The moisture transport resistance in the exchanger is determined by the boundary layer resistance on the humid air side, the membrane resistance, and the boundary

layer resistance on the dry air side. The boundary layer resistances of the different membranes are the same because the working conditions are the same. Therefore, the variations of K surely demonstrate that LiCl decreases resistance drastically at high content (above 2.5%) while reducing slightly resistance at low content.

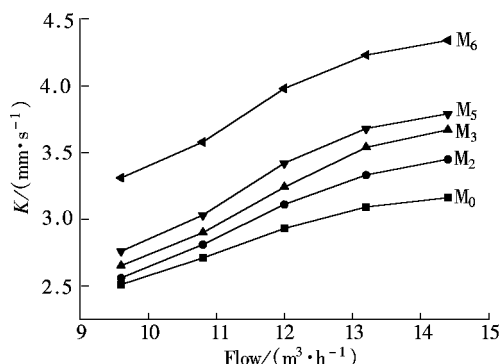


Fig. 4 Influence of LiCl content on total mass transfer coefficient

The effects of the LiCl content on the vapor permeation rate of PVDF membranes in different air flows are presented in Fig. 5. As observed, the addition of LiCl in the casting solution improves the water vapor permeation rate substantially. For example, the vapor permeation rate of a pure PVDF membrane in 12 m³/h flow is 1.87×10^{-5} kg/(m²·s), while that of membrane (M₂) with 1% LiCl increases to 2.45×10^{-5} kg/(m²·s). Furthermore, the vapor permeation rate increases with the increasing LiCl content. As is well known, the water vapor permeability depends on the hydrophilicity and the resistance of the membranes. In the case of a LiCl content below 2.5%, the increasing trend in permeation performances may be mostly due to the enhanced hydrophilicity of the membranes since LiCl increases K slightly, observed from Fig. 4. When the LiCl content increases to 3%, the membrane (M₆) shows the best moisture permeation performance due to the decreasing resistance and the increasing hydrophilicity. However, a 3% LiCl in the casting solution is not suggested because a high amount of LiCl enlarges pore size and drastically decreases mechanical strength.

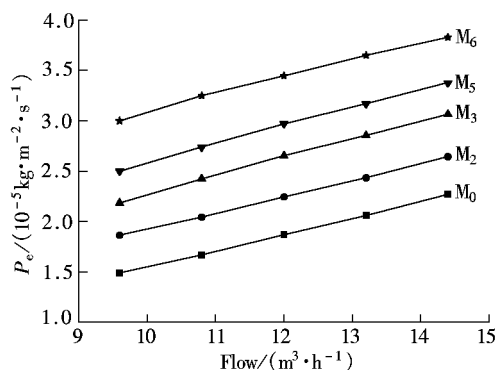


Fig. 5 Influence of LiCl content on permeation rate

3 Conclusion

Hydrophilic PVDF porous membrane is successfully prepared by blending PVDF with hygroscopic LiCl via the

phase inversion method. Contact angle measurements and sorption tests demonstrate that LiCl greatly improves the hydrophilicity of membranes. As LiCl content increases, water vapor permeation rate is improved significantly while the total mass transfer coefficient increases little and then is enhanced sharply at a high content (above 2.5%). This indicates that LiCl with high content enlarges pore size and decreases mechanical strength drastically. Therefore, 2.5% LiCl modified membrane is used as a good candidate for the support layer of composite membranes for dehumidification.

References

- [1] Pan C Y, Jensen C D, Bielech C H, et al. Permeation of water vapor through cellulose triacetate membranes in hollow fiber form[J]. *Journal of Applied Polymer Science*, 1978, **22** (8): 2307 – 2323.
- [2] Scovazzo P, Hoehn A, Todd P. Membrane porosity and hydrophilic membrane based dehumidification performance [J]. *Journal of Membrane Science*, 2000, **167** (2): 217 – 225.
- [3] Ye X H, Levan M D. Water transport properties of Nafion membranes. Part I. Single-tube membrane module for air drying[J]. *Journal of Membrane Science*, 2003, **221** (1/2): 147 – 161.
- [4] Chen G, Zhang X S, Wang J H, et al. Synthesis and characterization of soluble poly (amideimide)s bearing triethylamine sulfonate groups as gas dehumidification membrane material[J]. *Journal of Applied Polymer Science*, 2007, **106** (5): 3179 – 3184.
- [5] Upadhyay D J, Bhat N V. Separation of azeotropic mixture using modified PVA membrane[J]. *Journal of Membrane Science*, 2005, **255** (1/2): 181 – 186.
- [6] Anjali Devi D, Smitha B, Sridhar S, et al. Novel crosslinked chitosan/poly (vinylpyrrolidone) blend membranes for dehydrating tetrahydrofuran by the pervaporation technique [J]. *Journal of Membrane Science*, 2006, **280** (1/2): 45 – 53.
- [7] Zhang L Z, Wang Y Y, Wang C L, et al. Synthesis and characterization of PVA/LiCl blend membrane for air dehumidification[J]. *Journal of Membrane Science*, 2008, **308** (1/2): 198 – 206.
- [8] Aranda P, Chen W J, Martin C R. Water transport across polystyrenesulfonate/alumina composite membranes [J]. *Journal of Membrane Science*, 1995, **99** (2): 185 – 195.
- [9] Zhang L Z. *Dehumidification technology* [M]. Beijing: Chemical Industry Press, 2001. (in Chinese)
- [10] Singh N, Husson S M, Zdyrko B, et al. Surface modification of microporous PVDF membrane by ATRP[J]. *Journal of Membrane Science*, 2005, **262** (1): 81 – 90.
- [11] Nie F Q, Xu Z K, Huang X J, et al. Acrylonitrile-based copolymer membranes containing reactive groups: surface modification by the immobilization of poly (ethylene glycol) for improving antifouling property and biocompatibility[J]. *Langmuir*, 2003, **19** (13): 9889 – 9895.
- [12] Asatekin A, Menniti A, Kang S, et al. Antifouling nanofiltration membranes for membrane bioreactors from self-assembling graft copolymers [J]. *Journal of Membrane Science*, 2006, **285** (1/2): 81 – 89.
- [13] Zhu L P, Zhang X X, Xu L, et al. Improved protein-adsorption resistance of polyethersulfone membranes via surface segregation of ultrahigh molecular weight poly (styrene-alt-maleic anhydride) [J]. *Journal of Membrane Science*, 2007, **287** (2): 189 – 197.
- [14] Park J Y, Acar M H, Akthakul A, et al. Polysulfone-graft-poly (ethylene glycol) graft copolymers for surface modification of polysulfone membranes [J]. *Biomaterials*, 2006, **27** (6): 856 – 865.
- [15] Zhao Y H, Zhu B K, Kong L, et al. Improving hydrophilicity and protein resistance of poly (vinylidene fluoride) membranes by blending with amphiphilic hyperbranched-star polymer[J]. *Langmuir*, 2007, **23** (10): 5779 – 5786.
- [16] Zhang L Z. Mass diffusion in a hydrophobic membrane humidification/dehumidification process: the effects of membrane characteristics [J]. *Separation Science and Technology*, 2006, **41** (8): 1565 – 1582.

氯化锂对聚偏氟乙烯多孔膜的亲水改性

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摘要: 利用相分离法制备了亲水性聚偏氟乙烯(PVDF)-氯化锂共混膜, 通过接触角测量和水蒸气吸附实验评价了膜的亲水性, 并通过水蒸气渗透实验测试了总传质系数和水蒸气渗透速率。实验结果表明: 随着铸膜液中氯化锂含量的增加, PVDF膜的接触角明显降低, 同时, PVDF膜对水蒸气的吸附能力随之增加。当氯化锂质量分数低于2.5%时, 水蒸气在膜中的总传质系数略有增加, 当氯化锂质量分数高于2.5%时, 总传质系数明显增加, 而水蒸气在膜中渗透速率随氯化锂含量的增加而增加。因此, 氯化锂的加入可以显著提高PVDF膜的亲水性, 进而增强水蒸气的渗透性能。

关键词: PVDF多孔膜; 氯化锂; 亲水性; 除湿

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