

嘉南藥理科技大學專題研究計畫成果報告

薄膜分離系統之開發及其環境污染與資源回收之應用(II)
子計劃(一)：以光穿透法探討濕式相轉換法中溶劑交換速率對薄膜
結構之影響

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嘉南藥理科技大學教師專題研究計畫成果報告

子計劃(一): 以光穿透法探討濕式相轉換法中溶劑交換速率對薄膜結構之影響

The influence of liquid-liquid demixing rate on morphology of polysulfone membrane with wet phase immersion method

摘要

本研究擬以光穿透法探討以濕式成膜法製備離子性非對稱薄膜之成型機制與薄膜形態變化之關係。研究中分別將具離子交換能力之高分子溶液以不同鑄膜液組成於相轉換法成膜時進行光穿透實驗，探討濕式成膜過程中因鑄膜液組成及其成形過程改變中光透過率變化與非對稱薄膜型態及孔隙特性之關係。研究中考量溶劑與非溶劑組成變化，由光穿透法之觀察結果探討離子非對稱薄膜之孔隙與皮層形成是否受其組成變化之影響，並且透過高分子濃度變化、溶劑組成變化、離子交換高分子組成變化及成型條件差異之變因探討本研究所形成非對稱薄膜之差異特性，計畫結果將以動力學之觀點配合三相圖之方式加以解釋之結構與溶劑與非溶劑在凝聚槽中交換速率之差異並與薄膜結構相互印證，探討薄膜形成之主要控制因子並嘗試以溶劑添加使鑄膜液成膜時因成形路徑差異獲得所預期之薄膜結構。

Abstract

Different Polarity co-solvents additive in polymer solutions were casted by wet phase inversion technology for preparing asymmetric membranes. Chloroform (non-polar) and n-butanol (polar) were used as co-solvent in casting solution in polysulfone /N-methyl pyrrolidone(NMP) /water system. A delay liquid–liquid demixing can be observed in the case of non-polar solvent additive in casting solution during the formation of asymmetric membrane. The prepared asymmetric membranes own a dense skin layer and present a good separation performance. It was found that the polarity of

additive co-solvent in casting solution significantly influence demixing rate and lead to a different structure of skin layer. It was suggest that the polar solvent additive preferred to form a porous skin layer in polar coagulant solvent. The defect free dense skin layer can be formed with a non-polar solvent additive in polysulfone /NMP /water system.

Introduction

PV usually used to break the azeotropic point of water- alcohol mixtures ⁽¹⁻²⁾. Usually, the permeate transport in separation membranes were dominated by the thickness of selective skin layer of asymmetric membranes. A hydrophilic skin layer was used to improve the separation performance of pervaporation. However, a high degree of swelling usually induced a decrease in selectivity of membrane. Therefore, a suitable material and membrane formation process should be used to synthesize a selective skin layer of pervaporation membrane.

The hydrophilic sulfonated polysulfone can be prepared by sulfonation with choloro- sulfonic acid. In this study, hydrophilic sulfonated polysulfone was used as the material to prepare the asymmetric membranes with a selective skin layer by the wet phase inverse method. The delays demixing in wet phase inversion process were caused by the additive solvent and nonsolvent in the casting solution. The morphology and light transmitting measurement were made to identify the membranes's morphology and delay demixing behavior in membrane formation. The asymmetric membranes were applied to separate alcohol mixtures by pervaporation. Perselectivity and permeation flux of prepared membranes were measured to valuate the enhancement of sulfonation of membranes.

Results and discussion

Effect of Butanol additive on pervaporation properties and morphology of SPS membranes

The effect of butanol additive on the morphology change of SPS membrane was showed in Figure 1. As shown in Figure 1, the significant skin layers were formed and those membranes own figure-type structure sublayer. The sublayer thickness decreased with increasing the degree of sulfonation of polysulfone. We also measured the skin layer thickness to clarify the influence of butanol additive on the skin layer formation. **Figure 2** showed the skin layer thickness of those additive membranes. It was indicated that the skin layer thickness increased with increasing the degree of sulfonation from 3.75 to 4.5 μm . Those surfaces of skin layers of SPS membrane were also

observed by SEM to make sure they are defect free. It was found that there are no observable pores on the skin. It was indicated that the dense skin were formed by this wet phase inversion process. Figure 3 showed the effect of degree of sulfonation of polysulfone on pervaporation properties with butanol additive in casting solution. It can be seen that the permeation flux almost constant and the perselectivity decreased with increasing degree of sulfonation. This result is not consistent with the morphology observation. It was implied that even the skin layer had formed in wet process, there are no obvious defects on the surface and those defect lead to a decrease in perselectivity of SPS membranes.

Effect of chloroform additive on pervaporation properties and morphology of SPS membranes

In order to identify the additive co-solvent effect on the morphology of SPS membrane, the non-polar solvent (chloroform) was added into casting solution and casted the membranes by the same procedure. As shown in Figure 4, the obvious skin layers were formed and those membranes own the same figure-type sub-layer. We also measured the skin layer thickness of those membranes to clarify the influence of chloroform additive on the structure skin-layer. **Figure 5** showed the skin layer thickness of those additive membranes. It can be seen that that the skin layer thickness increased with increasing the degree of sulfonation from 2.5 to 4 μm . It was indicated that the chloroform additive in casting solution also formed an integral skin layer but less than the n-butanol additive membranes. It was expected that that the similar separation performance of those membranes as the performance of membranes with butanol additive. Therefore, the pervaporation properties of those membranes were also made to evaluate the separation performance. Figure 6 showed the effect of sulfonation on pervaporation properties with chloroform additive. It can be seen that both of the permeation flux and the perselectivity increased with increasing the degree of sulfonation with 8 wt% chloroform additive. The increase in degree of sulfonation increased the hydrophilicity of SPS. Therefore, the increase in permeation flux was enhanced by the improvement of hydrophilicity of SPS membranes with various degree of sulfonation. It should be note that the perselectivity of SPS membrane with chloroform additive also increased with the degree of sulfonation. There is no decline in perselectivity with increasing in sulfonation. It was implied that the defect free skin layer was formed in this wet process and those dense skin layers lead to an increase in perselectivity of SPS membranes with chloroform

additive. It can be found that the polar butanol additive into casting solution induced a poor permeability of SPS membranes. However, the non-polar chloroform additive into casting solution enhanced both permeation flux and permeability of SPS membrane. Though, the butanol additive membranes almost own the same morphology as the chloroform additive membranes. However, the permeability of those membranes were significantly different. It was proposed that the defects on skin layer dominated their permeation properties. Therefore, a possible reason to explain these skin structures should be found.

Light transmission measurement

The defect free skin layer membranes can be prepared by two membrane formation mechanisms⁽⁵⁾. Dense skin layers with defect free of those membranes were prepared by a delay demixing process and porous sublayers were formed by instantaneous demixing process. In this work, the co-solvent additive in casting solution was used to prepare the asymmetric membrane by delaying the demixing process in membrane formation. For the purpose of clarifying the demixing process in wet phase inversion process, the light transmission measurements were made. Figure 7 showed the light transmission measurement with the same volume fraction of co-solvent additive in membrane formation by wet phase inverse process. It can be seen that the polar butanol added into the SPS/NMP casting solution slightly delay the demixing rate. On the other hand, the chloroform added into the casting solution significantly delays the demixing process in water bath. The delay demixing process usually contributed by the mass transfer rate of casting solution and coagulant before polymer was completely precipitated in membrane formation. Based on the observation of morphologies and pervaporation measurements, it was found that the delay demixing in chloroform additive system leads to a similar morphology as the butanol additive system. However, the skin layer of chloroform additive system is denser than the butanol additive because of the longer time demixing in membrane formation process. It was concluded that the non-polar cosolvent additive in casting solution favors following the delay demixing process and forms a denser skin layer of asymmetric membranes.

Conclusion

The delay demixing process by non-polar solvent additive in SPS/NMP system can be found. The non-polar cosolvent additive in casting solution promotes the delay demixing process and forms a

denser skin layer of asymmetric membranes. The dense skin layer of asymmetric membranes can be prepared by chloroform/SPS/NMP casting solution in water coagulant bath and those membranes showed a good pervaporation performance in separation water/ethanol mixture.

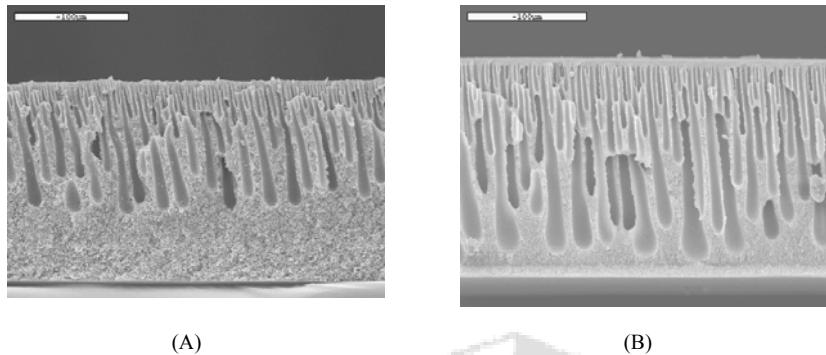


Figure 1. The cross section of sulfonic PSF membrane with 12 wt % butanol additive. Degree of substitution with SO_3H : (A) 0.25 (B) 0.92. In ; 25 wt % PSF/NMP. Coagulant : H_2O Temperature : 25

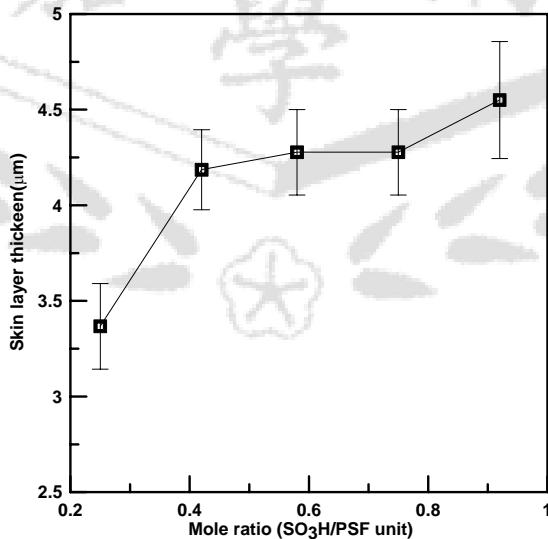


Figure 2. Effect of degree of sulfonic substitution on the skin layer thickness of asymmetric PSF membranes. In 25 wt % PSF/NMP. Coagulant : H_2O Temperature : 25

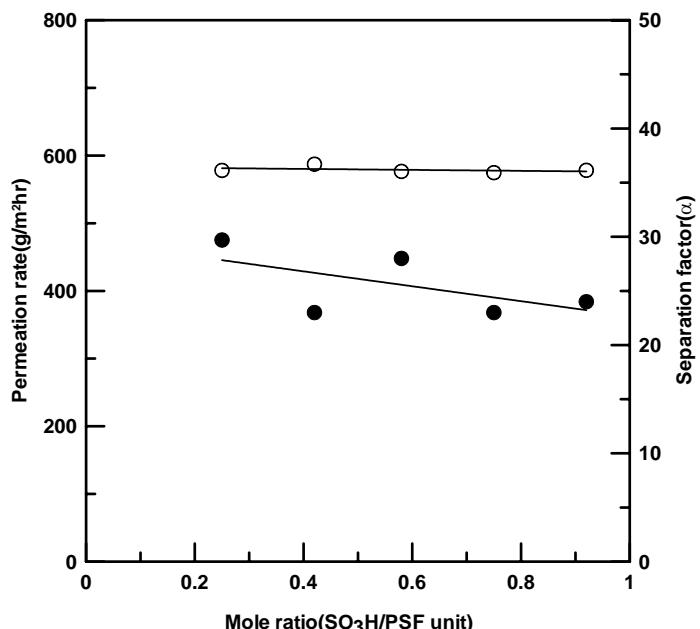


Figure 3. Effect of degree of sulfonic substitution on pervaporation performance of asymmetric sulfonated membrane for 90 wt.% ethanol solution in feed at 25

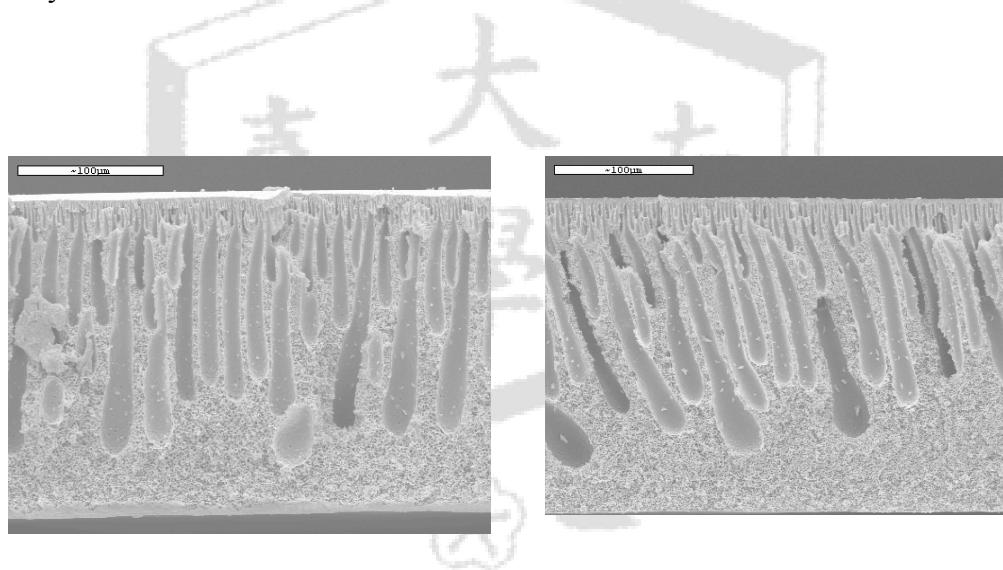


Figure 4. The cross section of sulfonic PSF membrane with 12 wt % chloroform additive. Degree of substitution with SO₃H : (A) 0.25 (B) 0.92. In ; 25 wt % PSF/NMP. Coagulant : H₂O Temperature : 25

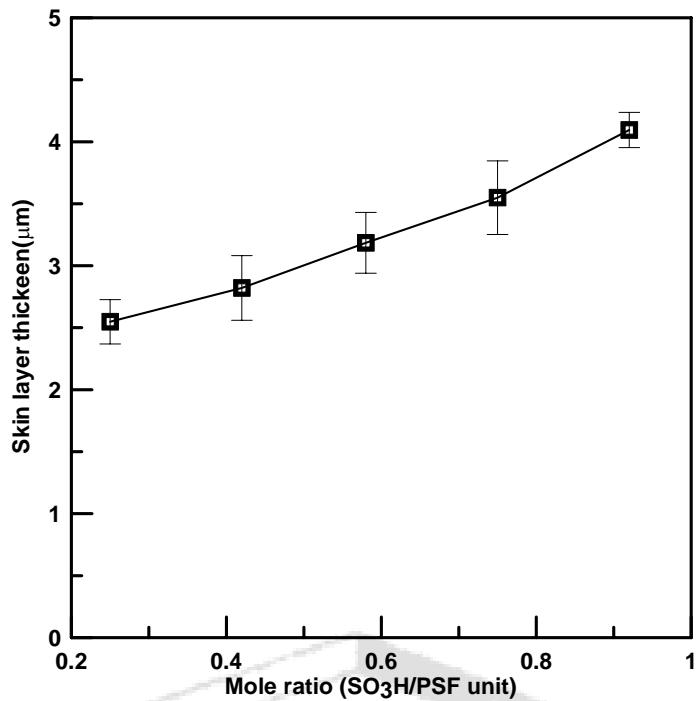


Figure 5. Effect of degree of sulfonic substitution on the skin layer thickness of asymmetric SPSF membranes.

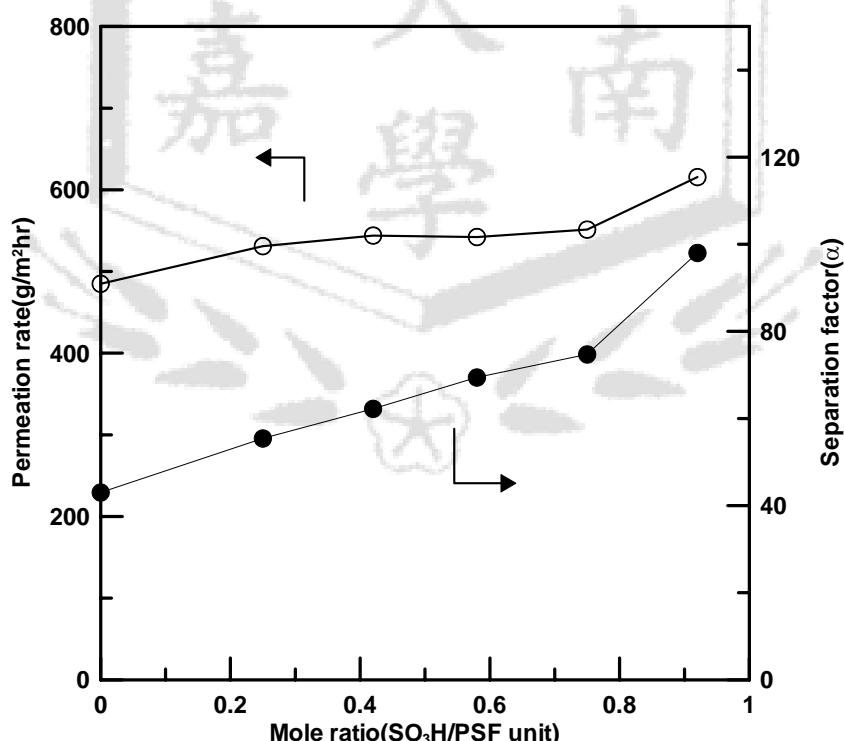


Figure 6 Effect of degree of sulfonic substitution of polysulfone on pervaporation performance of asymmetric SPSF membrane for 90 wt.% ethanol solution in feed at 25

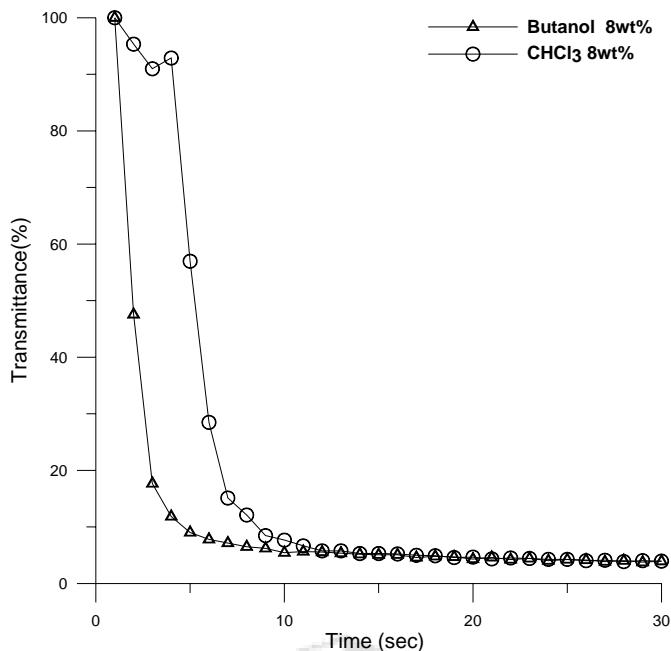


Figure 7 Effect of co-solvent additive on light transmittance of asymmetric SPSF membrane at 25

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