

Morphology Change of Biaxially Oriented Polytetrafluoroethylene Membranes Caused by Solvent Soakage

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ABSTRACT: The morphological changes of expanded polytetrafluoroethylene (ePTFE) membrane caused by solvent soakage were investigated in this study. The results demonstrated that the wettable solvent with low contact angle towards PTFE membrane can introduce huge stress to the ePTFE membrane and make the membrane shrinkage, and the stress is generated in the solvent evaporation procedure. The pore size and membrane dimension shrinkage of ePTFE membrane improved with the decrease of the solvent contact angle and surface tension.

For ethanol and isopropanol with contact angle of 23° and 20°, the membrane thickness shrinkness are 15.0% and 16.7%, respectively. The evaporation-induced stress towards the ePTFE membrane also increases with the decrease of the solvent contact angle to the ePTFE membrane. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 1464–1468, 2011

Key words: expanded polytetrafluoroethylene membrane; contact angle; surface tension; evaporation-induced stress

INTRODUCTION

The biaxially oriented PTFE microporous (ePTFE) membranes displays many highly desirable bulk and surface properties, e.g., excellent water proof and breathable capabilities, good charge storage stability, electrical insulation properties, and extreme frictional resistance and low surface energy, based on the low polarity of the C-F bond. These properties are desired in many applications as an important key material like membrane separation and environmental protection materials,¹ functional clothing materials,² as well as the piezoelectric and charge storage field.^{3–6} At the same time, ePTFE membrane has up to 85% or more porosity, more than 50 MPa mechanical strength of its body PTFE materials, and high thermal stability, chemical inert-

ness, can composite with functional polymer materials or inorganic materials to form structural stability, with high functional components composite materials. These composite materials have a broad application prospect in the field of cosmetic medicine^{7–9} and functional composite film.^{10,11} The structural stability and mechanical properties of the functional composite ePTFE membrane mainly depends on the ePTFE membrane matrix; furthermore, the structural change of the ePTFE matrix in the preparation process of composite material have an important bearing to the materials composite.

Many studies have shown that there are still many factors that can change the physical structure of the ePTFE matrix material. High-temperature heat treatment has been proven to have an important influence to the microstructure of the ePTFE membrane. Zhang et al.¹² have studied the morphology of the ePTFE membrane by use of scanning electron microscopy, they found that the structural stability of ePTFE membrane need a process of heat treatment, the filamentous fibers of the porous membrane without the heat treatment will shrink in the storage process, then it will change the pore morphology of the membrane; Kitamura et al.¹³ have studied the influence of heat treatment to the structure of porous membrane and found that heat treatment in 200–320°C can also lead to the contraction of ePTFE membrane pore. Other surface treatment methods, for example plasma surface

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treatment¹⁴ or grafted chemical groups not only can improve the hydrophilicity of ePTFE membrane,^{15,16} but also can lead to the structure changes of porous membrane. In particular, the preparation of plastic body medicine or other functional composite film with ePTFE membrane as basal body multiuse wet-chemical methods, then it will all use a variety of solvents; however, intrinsic nature of the solvent will affect the microporous structure change of ePTFE membrane, accordingly influence the structure stability and superior property of the ePTFE composite membrane.

This article reports our research on pores and microstructural changes behavior of the ePTFE porous membrane in the solvent. The mechanism of the ePTFE porous membrane shrinkage in related to the surface tension and contact angle of the solvent towards to the PTFE also discussed in detail.

EXPERIMENTAL

Materials

The biaxially oriented PTFE microporous (ePTFE) membranes used were commercially received from Shanghai Dagong Comp. China, with a porosity of about 85%. The mean pore size of the ePTFE membranes was about 0.4 μm , with a thickness of 15 μm . All the solvent used were obtained from Sinopharm Chemical Reagent.

Structure shrinkage of ePtfE porous membrane with solvent treatment

In the experiment, the biaxially oriented PTFE microporous (ePTFE) membranes were mounted on 10 cm \times 10 cm plastic frames, the thickness of the labeled point of ePTFE membrane, d , were menstruated by use of Film Thickness Tester (CH-1-B, accuracy 0.1 μm , Shanghai six Ling Instrument Factory, China). After that, the porous ePTFE membrane were immersed into solvent and kept for 10 min. The membranes were then air-drying at 25°C for 24 h. The membrane thicknesses of the immersed membrane at the labeled points were measured as d' . The change ratio of the porous ePTFE membrane, η , was calculated based on the relationship between d and d' :

$$\eta = (d - d')/d \times 100\% \quad (1)$$

Methods

Surface and cross sections of the composite membranes were examined by scanning electron microscopy (SEM, JEOL JSM-5610LV). The samples were Au-sputtered under vacuum before the SEM examination. The wetting property of different solvent in the surface of PTFE membrane was analyzed

using the sessile drop method (Automatic Contact Angle Meter, Kyowa Interface Science, Japan).

The *in-situ* shrinkage stresses of the ePTFE membrane generated by the solvent soakage and evaporation were measured by the Electromechanically Universal Testing Machine (WDW-1C). The chamber was fitted on the horizontal rail of the machine load frame. During the test, the samples were cut to spindle shape with dimension of 1 cm \times 10 cm, and two ends of the sample were clamped by the claws of the testing machine. Before data taken, the claws were shifted very slowly by set the strain rate as 0.1 mm/min till the samples were stretched and absolutely paralleled to the clamps. Then various solvent were soaked to the membrane by contact the samples with the storage solvent and recorded the *in-situ* stress data. After the soakage, the *in situ* shrinkage stresses of the ePTFE membrane generated by the solvent evaporation were record by removing the storage solvent, and let the sample air-dried under room temperature.

RESULTS AND DISCUSSION

Pore structure shrinkage effect of ePtfE porous membrane with solvent treatment

Figure 1 depicts the SEM micrographs for the ePTFE membrane immersed in water, ethanol, or isopropanol for 10 min, and then air-drying at 25°C for 24 h condition. For the purpose of comparison, the SEM micrograph of the as-received ePTFE membrane is also shown in Figure 1. It is observed that the micrograph microstructure of the ePTFE membrane have little structure change after immersing in the water [Fig. 1(b)] with the similar pore size of $\sim 2 \mu\text{m}$ and porosity of $\sim 85\%$. However, in the case of immersing in ethanol or isopropanol [Fig. 1(c,d)], significant pore diameter shrinkage was clearly visible on the morphologies of the ePTFE membrane. The shrinkage of the pore diameter is most likely due to the physically interfacial interaction between the ePTFE fibers and the solvent since the ePTFE is inherent chemically inert in the alcohol. According to the pore size shrinkage, clearly, the geometrical dimension shrinkage (the thickness and porosity reduction) of the ePTFE membrane was also presented during the experiment. Compared to the as-received state, the membrane thickness and porosity of the ePTFE membrane immersing in isopropanol and then air-drying for 24 h has a significant decrease of 16.7 and 3%, respectively.

Influence of the solvent on the structure shrinkage of the ePtfE membrane

The wettabilities of solvents on the ePTFE porous membrane were investigated to understand the interfacial interaction between the solvent and PTFE

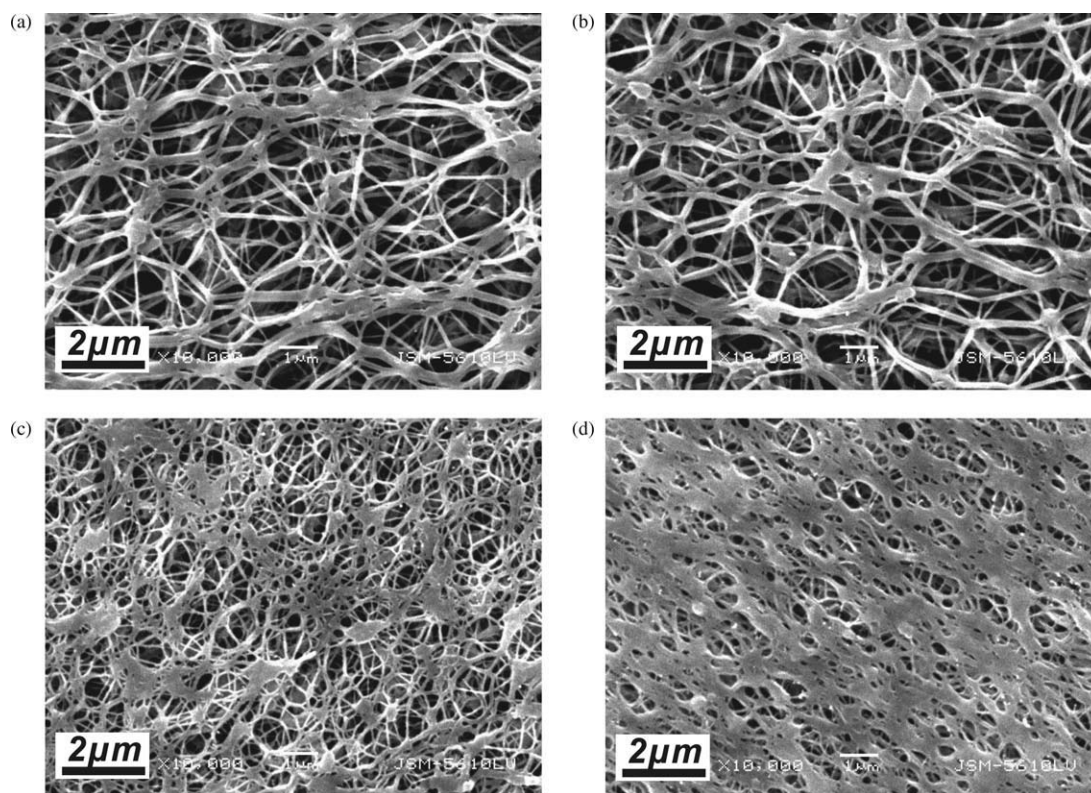


Figure 1 SEM micrographs for the ePTFE membrane (a) as received and immersed in water (b), ethanol (c), isopropanol (d) for 10 min, and then air-drying at 25°C for 24 h condition.

membrane. It is found that solvents with low wettability, such as *N*-Methyl pyrrolidone (NMP) and D.I water, are difficult to permeate into the porous structure of the ePTFE membrane, resulting in a suspending state of the ePTFE membrane in the solvent. Thus, the membrane thickness and pore diameter of the ePTFE membrane have little change after the immersion. While for other candidate that have high wettability to the PTFE membrane, such as methanol, ethanol, isopropanol, toluene, and *N,N*-dimethylformamide (DMF), the solvent can permeate the membrane in short time and introduce pore size and membrane thickness shrinkage to the ePTFE membrane. To demonstrate the influence of wettabilities of the solvent on the structure shrinkage of the ePTFE membrane, the contact angle of various solvent on porous ePTFE membrane and the thickness shrinkage of the ePTFE membrane were tested, and the results are displayed in Figure 2. The results suggest that the interfacial interaction depends much on the contact angle of the solvent on the porous ePTFE membrane. Solvent with large contact angle can not change the membrane microstructure and the membrane thickness. For the solvent that can wet the PTFE membrane, the membrane thickness shrinkage increase with the decrease of the contact angle. For the solvent with contact angle close to 90°, e.g., DMF (95°, $\cos \theta = -0.1$), also can contact to the ePTFE membrane and make the thickness

shrinkage. The reason is most likely due to the extension of the solvent on the PTFE fibers is dependent on the free energy change (ΔF) of the

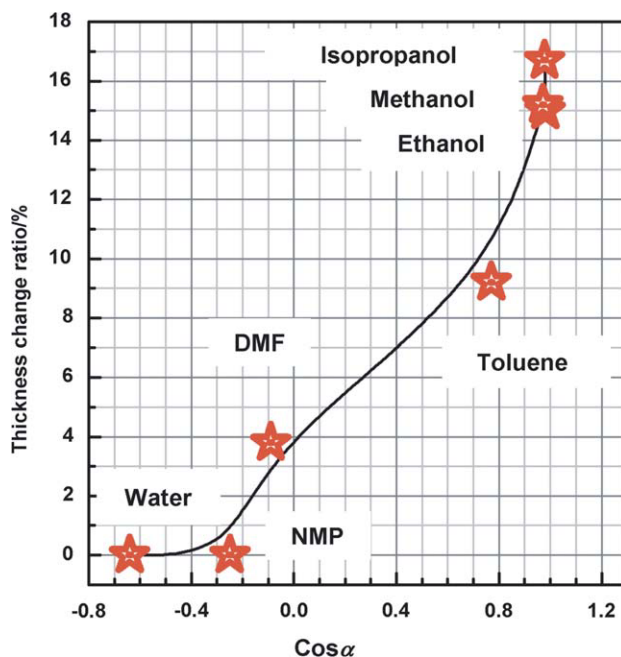


Figure 2 The thickness shrinkage of the ePTFE membrane as a function of the contact angle of various solvent. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com)].

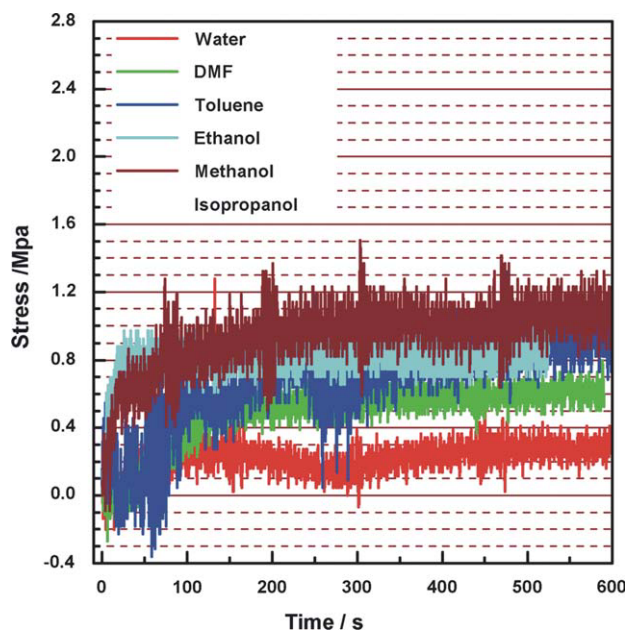


Figure 3 In-situ shrinkage stresses of the ePTFE membrane induced by solvent evaporation in a long-term period. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

solvent on the PTFE fiber. The change of the free energy change (ΔF) can be written as:

$$\Delta F = -\gamma_{gl}(1 + R_w \times \cos \theta) \times A \quad (2)$$

where γ_{gl} is responsible for the surface tension of the solvent, R_w is the roughness of the ePTFE membrane, θ is the contact angle, A is the geometrical area of the solid-liquid interface. If $\Delta F > 0$, the solvent cannot spontaneously spreading on the PTFE fiber. Thus, the interaction between the solvent and the PTFE fiber is very little. Inversely, if $\Delta F < 0$, the solvent spontaneously spreading on the PTFE fiber and introduce membrane thickness and microstructure change to the ePTFE membrane.

In eq. (2), the contact angle of the solvent on the PTFE membrane determines if properties of ΔF . If $\Delta F < 0$, the $\cos \theta$ can be written as:

$$1 + R_w \times \cos \theta > 0 \quad (3)$$

For the ePTFE membrane, the roughness is about 2π . If $\cos \theta \geq 1/2\pi$ ($\theta < 99^\circ$), the solvent can wetting the ePTFE membrane, and make the membrane thickness and microstructure shrinkage.

The physically mechanism of the solvent with high wettabilities shrinkage the ePtfE structure

To understand the shrinkage mechanism of the ePTFE membrane under solvent conditions, *in situ* shrinkage stresses of the ePTFE membrane were tested during solvent soakage and evaporation procedure. The results indicate the shrinkage stresses gen-

erated by various solvent soakages are close to 0, suggesting that pore size and membrane dimensional shrinkage can not be generated by the solvent soakage. The *in situ* shrinkage stresses of the ePTFE membrane induced by solvent evaporation procedure are displayed in Figure 3. The results demonstrated that tremendous stress is introduced to the ePTFE membrane during the wettable solvent evaporation period. While for the solvent with low wettability, such as DMF and D.I. water, the evaporation-induced stress is featureless, implying that the evaporation-induced stress is the critical reason that makes the porous membrane shrinkage. For the solvent with low wettability, the evaporation-induced stress increased with the increase of the solvent contact angle to the ePTFE membrane. The evaporation-induced stress by the toluene (contact angle 42° , $\cos \theta = 0.743$) is about ~ 0.6 Mpa. However, this value increased to 0.79, 0.8, and 1.2 Mpa for the ethanol, methanol, and isopropanol, respectively, with the contact angle of 23° , 23° , and 20° . It is also should be noted that the evaporation-induced stress by the wettable solvent increased slowly in the initial state and then reached to a platform during the long-term solvent evaporation period, suggested a unrecoverable structure change, e.g., pore structure and membrane dimensional shrinkage of the ePTFE membrane.

Figure 4 displays curves of evaporation-induced stress, as well as the membrane thickness shrinkage as function of the surface tension of the wettable solvent. The results clearly revealed that the evaporation-induced stress and the membrane thickness shrinkage

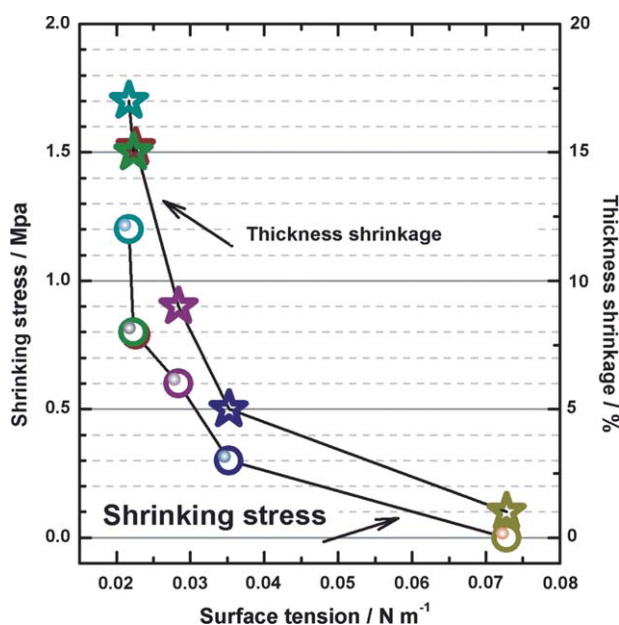


Figure 4 Evaporation-induced stress and membrane thickness shrinkage of the ePTFE membrane as function of the surface tension of the wettable solvent. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

improved with the decrease of surface tension of the solvent. The similar trends of the evaporation-induced stress and the membrane thickness shrinkage curves demonstrated the evaporation-induced stress is the critical reason that makes the porous membrane shrinkage. In the case the wettable solvent, a critical point of surface tension at ~ 0.035 mN/m displays in the curves, below this point the evaporation-induced stress and the membrane thickness shrinkage increase sharply with surface tension decrease, implies huge shrinkage stress generated by the wettable solvent at this condition. Figure 4 displays curves of evaporation-induced stress, as well as the membrane thickness shrinkage as function of the surface tension of the wettable solvent. The results clearly revealed that the evaporation-induced stress and the membrane thickness shrinkage improved with the decrease of surface tension of the solvent. During the solvent evaporation process, the reduce the surface solvent on the liquid concave meniscus increase the solid-vapor interfacial energy and destroy the PTFE-solvent-gas three phase force equation on the solid-liquid interface based on the Young's Equation:

$$r_{sg} - r_{sl} - r_{gl} \cos \theta = 0$$

where γ_{sg} , γ_{sl} , and γ_{gl} are responsible for the solid-vapor interfacial energy, solid-liquid interfacial energy, and surface tension of the solvent, respectively. In the transient evaporation, the flexible PTFE fibers must shift to the liquid direction to balance the surface energy and reduce the liquid tension. Thus, the solvent evaporation introduces pore diameter and structure shrinkage to the porous PTFE membrane. The trend of the evaporation-induced stress improves with the decrease of surface tension also implies that the shrinkage of the membrane is dependent on the wettability of the solvent. Because of the very low surface tension of the PTFE fibers, solvent with low surface energy is benefit to spread solvent on the PTFE fibers, resulting in low contact angle and excellent liquid spread. The less the contact angle represents the greater contact interface between the PTFE fiber and the solvent, and introduce great structure shrinkage to the ePTFE membrane. In this case, the evaporation-induced stress is a reflection of the membrane structure shrinkage based on the stress-strain relationship of the flexible membrane.

CONCLUSIONS

Morphological changes of ePTFE membrane caused by solvent soakage were investigated in related to the surface tension and contact angle of the solvent towards to the PTFE membrane. The results demonstrated that the wettable solvent can introduce huge

stress to the ePTFE membrane and make the membrane shrinkage, for detail:

1. ePTFE membrane structure keep stable in the high contact angle solvent, such as *N*-methyl pyrrolidone (NMP) and D.I water. In the case of wettable solvent, low contact angle towards PTFE membrane, such as ethanol, isopropanol, toluene, and *N,N*-dimethylformamide (DMF), can reduce pore size and shrinking the membrane dimension of the ePTFE membrane.
2. The pore size and membrane dimension shrinkage of ePTFE membrane improved with the decrease of the solvent contact angle and surface tension. For ethanol and isopropanol with contact angle of 23° and 20° , the membrane thickness shrinkage are 15.0 and 16.7%, respectively.
3. The evaporation-induced stress towards the ePTFE membrane increased with the decrease of the solvent contact angle to the ePTFE membrane. The evaporation-induced stress by the toluene (contact angle 42° , $\cos \theta = 0.743$) is about ~ 0.6 Mpa. The evaporation-induced stress values are 0.8 and 1.2 Mpa for the ethanol and isopropanol, respectively.

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