J Mater Sci (2010) 45:6569–6573
DOI 10.1007/s10853-010-4475-7

A novel method to prepare hydrophobic poly(tetrafluoroethylene) membrane, and its properties

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Received: 12 November 2009 / Accepted: 5 April 2010 / Published online: 1 October 2010

Abstract Hydrophobic poly(tetrafluoroethylene) (PTFE) flat-sheet membranes were prepared by a novel method with polyvinyl alcohol (PVA) as membrane carrier. Factors affecting PTFE membrane pore structure and mechanical properties such as sintering temperature, sintering state, and the simulate model were investigated. Results show that it was better to form pore structure at the first sintering stage. Morphologies of membranes were observed by scanning electronic microscopy (SEM). Membrane microvoids among the fibrils net nodes were loose by fixed setting sintering while compact by relax setting sintering. Chemical constitution and thermal stability of PTFE/PVA blend membrane after sintering (m-PTFE) and PTFE membrane were investigated, and no obvious difference in chemical constitution could be found between m-PTFE and PTFE membranes. The m-PTFE membranes obtained are still strong hydrophobic by the determination of contact angle to water.

Introduction

In membrane separation fields, hydrophobic porous membranes are widely applied in membrane distillation (MD), osmotic distillation (OD), supported liquid membrane (SLM), and membrane contactor (MC) [1]. As we know, there are many techniques producing polymer porous membranes, such as sintering process, L–B phase inversion method, melting–stretching method, thermally induced phase separation (TIPS), and so on [2]. As for hydrophobic membrane, polypropylene (PP), poly(vinylidenefluoride) (PVDF), and poly(tetrafluoroethylene) (PTFE) are the ideal materials for their strong hydrophobic properties [3, 4]. Currently, the commercial hydrophobic PP porous membrane is produced by melting–stretching method because there is no appropriate solvent to dissolve it [5, 6]. PVDF membrane can be manufactured by L–B method and TIPS to get homogeneous micropores and size-controllable structure [7].

Poly(tetrafluoroethylene) exhibits many unique characteristics such as outstanding thermal and chemical resistance, high hydrophobicity, low surface friction, and high fracture toughness. However, despite this exceptional combination of properties make PTFE a prime material for demanding membrane application, especially industrial filters, MD [8, 9], due to its ultra-high weight-average molar masses (typically $>10^7$ g/mol), standard PTFE grades have a very high melt viscosities, most often exceeding 10^{11} Pa s [10–12], which prohibits common thermoplastic-polymer processing techniques such as injection molding and melt spinning. Furthermore, there is no solvent to dissolve PTFE either. Therefore, PTFE membrane cannot be produced by such methods used for PP and PVDF [9]. Presently, the commercial PTFE porous flat-sheet membranes are mainly manufactured by biaxial stretching technology, which is significantly important for the film forming in the node-fiber micropore structure [13].

Guo [14] spun PTFE fiber through PTFE suspension with PVA as the carrier. However, except for patent, few reports could be seen for PTFE membrane preparation. In this article, a novel method was used to produce PTFE membrane and the feasibility of it and properties of membranes obtained were investigated.

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Experimental

Materials

The PTFE concentrated suspension is a commercial product (3F new materials co., LTD. Shanghai) designed as FR301B, with characteristics shown in Table 1. Polyvinyl alcohol (PVA) is purchased from Sanwei Group co,. LTD. Shanxi. Type: 2099 (polymerization degree: 2000; alcoholysis: 99%).

Membrane preparation

Polyvinyl alcohol powders were dissolved in distilled water at 90 °C, and then added PTFE dispersion into PVA solution, and was kept stirring until PTFE suspension was dispersed homogenously. In the process, the polymer solution was cast into films on a clean and smooth glass plate. The films were then immersed in pure ethanol at 5 °C. The PTFE/PVA membranes were then obtained. Afterward, the PTFE/PVA membranes were sintered at different temperatures with different sintering states, after which m-PTFE membranes were finally obtained. Pure PTFE membranes were prepared by pressing film after the PTFE suspension breaking emulsion, which is denoted as P-PTFE membrane. The sintering temperature is 340, 360, and 380 °C, respectively. The sintering states included fixed and relax sintering.

Method and measurements

FTIR spectra

IR spectra of the samples were recorded with Bruck Tensor37 IR spectrophotometer in a wave-number range from 400 to 4000 cm^{-1}. The spectral resolution was 4 cm^{-1}. Samples for IR analysis (in the transmission mode) were prepared at 25 °C in the form of KBr pellets.

TG

Thermal properties were evaluated via TGA (NETZSCH, STA409PC). It was investigated under N_2 atmosphere, and the thermal program was set at a heating rate of 10 °C/min from 100 to 700 °C. The weight of samples used in all measurements was 5–10 mg.

Contact angle

The contact angles of all the samples were measured by an optical contact angle meter (Jinshengxin Inspection instrument Co., Ltd., model JYSP-180). The measurements were carried out at 25 °C with 40–50% relative humidity. A water droplet was dropped on the sample surface from a distance of 5 cm by vibrating the tip of a micro-syringe. The diameter of the water droplet was about 1 mm, lasting for 10 s after the droplet was dropped on the sample surface. A lens and a source light were used to create the drop image on a screen. The contact angle was determined with the projected drop image. Five different spots for each sample were measured. The average value of the five spot as the contact angle of the membrane sample was chosen.

Porosity

The porosity was determined by gravimetric method [15], which determined the weight of liquid contained in the membrane pores. We used isopentane whose surface tension was 15×10^{-3}N/m (20–25 °C) for its low surface energy. Formula 1 is used to calculate ε of the membrane,

$$\varepsilon = \frac{(w_1 - w_2)/D_1}{(w_1 - w_2)/D_1 + w_2/D_\mathrm{p}} \tag{1}$$

where w_1 is the weight of the wet membrane, w_2 the weight of the dry membrane, D_1 the isopentane density ($D_1 = 0.62$ g/cm^3), and D_p is the polymer density ($D_\mathrm{PTFE} = 2.20$ g/cm^3).

Scanning electron microscopy

Morphologies of the membranes were examined using scanning electron microscopy (SEM, FEI, Quanta200). The dry membrane samples were frozen in liquid nitrogen, and then fractured to expose the cross-sectional areas. These samples were gold-coated and viewed with SEM.

Result and discussion

Chemical composition

The chemical compositions of the membranes were investigated by a transmission FTIR spectrophotometer. In Fig. 1,

Table 1 Characteristics of PTFE suspension

Solid content (wt%)	Nonionic surfactant content (wt%)	Average particle size (μm)	Viscosity (Pa S)	Density (g cm^{-3})	pH
60	5	0.19	25×10^{-3}	2.20	9

Note: Typical values

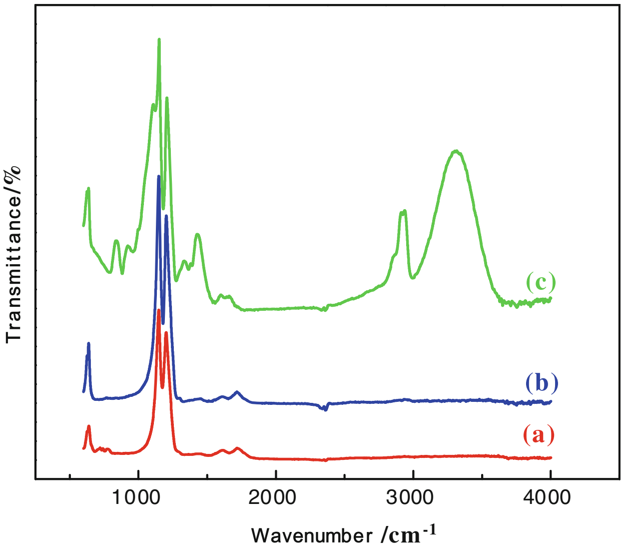

Fig. 1 FTIR spectra of samples: (*a*) P-PTFE, (*b*) m-PTFE, (*c*) PTFE/PVA, before sintering

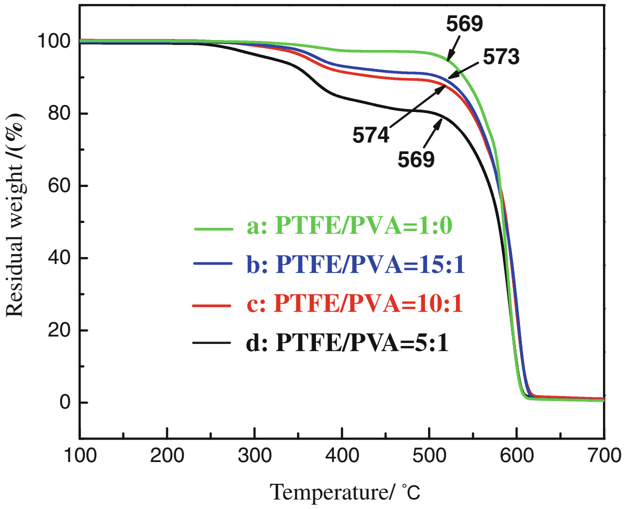

Fig. 2 Thermogravimetry curves for different ratio of m-PTFE membranes

Table 2 Water contact angle of membrane samples

Sample	Test time					Average value
	1	2	3	4	5	
PTFE/PVA	59.06°	60.85°	66.79°	66.92°	62.39°	63.20°
m-PTFE	111.31°	107.51°	112.26°	110.29°	102.68°	109.21°
P-PTFE	117.84°	118.62°	118.18°	121.15°	120.34°	119.23°

the two bands near 1250 and 1149 cm^{-1} are assigned to the C–F stretching vibrations of PTFE, and 638 cm^{-1} band is the CF_2 rocking or wagging bending vibrations of PTFE [16]. The two bands around 2937 and 3315 cm^{-1} are characteristic for PVA (Fig. 1c) [17], while in Fig. 1b, they disappeared after sintering, and the spectra are similar to P-PTFE (Fig. 1a); therefore, there is no obvious difference in chemical constitution compared with P-PTFE.

Thermal properties

PTFE/PVA before sintering: $a = 1/0$; $b = 15:1$; $c = 10:1$; $d = 5:1$. In this article, the thermal properties of different ratio of PTFE/PVA membranes were investigated. Figure 2 shows the TG curves of various samples. The weight-loss transition of the P-PTFE polymer began at 569 °C and was substantially completed at 617 °C (shown in Fig. 2a). Each TG curve of PTFE/PVA membranes can be divided into two regions (Fig. 2b–d). In the first region (about 250–400 °C), the weight-loss transition may be due to the decomposition of PVA. The second region corresponds to decomposition of PTFE, and there was no obvious difference in the initial decomposition temperature compared with P-PTFE. Thus, the method producing PTFE membrane with PVA as membrane carrier does not change the thermal stability of PTFE and the membranes obtained still exhibit good thermal stability.

Hydrophobic property

Poly(tetrafluoroethylene) is the polymer with lowest surface energy, having strong hydrophobic property. The average water contact angle is 114–115°; the balance water absorption rate is less than 1%. PVA is hydrophilic polymer with −OH, which will form hydrogen bond with water molecule. The water contact angles of the samples were shown in Table 2.

Results showed that the average water contact angle of PTFE/PVA membrane is 63.20° because of the hydrophilic property of PVA. After PVA was removed, the average water contact angle of m-PTFE membrane rises to 109.21° exhibiting strong hydrophobic performance. The P-PTFE membrane has the highest water contact angle (119.23°).

This reveals that the method used for producing PTFE membrane with PVA as the membrane carrier would not change the hydrophobic property of PTFE. Figure 3 shows the water contact angle of the membrane sample.

Effect of sintering condition on the membrane properties

Sintering temperature

Sintering temperature is a significantly important process parameter in the porous membrane manufacture through

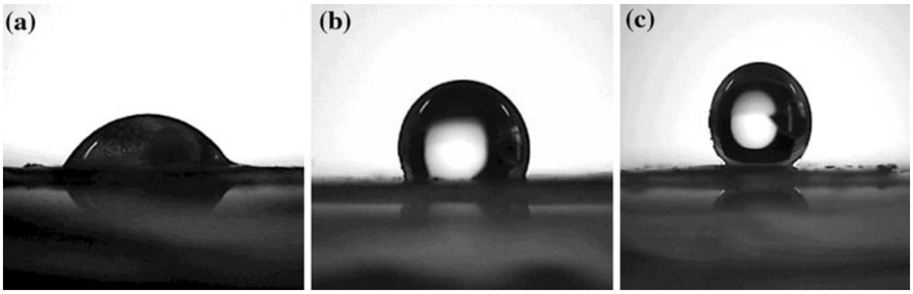

Fig. 3 Water contact angle photographs of membranes obtained. **a** PTFE/PVA membrane, **b** m-PTFE membrane, **c** P-PTFE membrane

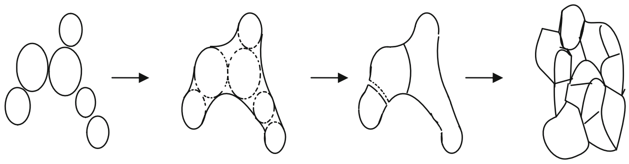

Fig. 4 Schematic diagram of membrane change in the sintering process

sintering method [18]. The sintering process can be described in Fig. 4, which could be divided into three stages. As for porous membrane, the first sintering stage is most important, during which the resin adheres with each other and the interspaces form the pore structure. After this stage, the membranes have not only good mechanical performance but also porous structure. With the temperature increasing, much changes took place in membrane structure and the porosity of membrane decreases obviously. During the last sintering stage, the membranes became compacted.

Figure 5 reveals the influence of sintering temperature to the membrane porosity. The porosity dropped while breaking tenacity elevated with sintering temperature increase. In PTFE/PVA membrane, PTFE resins homodisperse in PVA membrane carrier. According to the TG result shown in Fig. 2, the sintering temperature rises to about 340 °C, which is called the first sintering stage. In this stage, PVA has been removed; PTFE resins start to leave the contact with each other although the adherence was a bit poor. When the sintering temperature rises, the adherence among PTFE resins became much better, as is shown of both breaking tenacity and dropping porosity, and after sintering temperature rises to 370 °C, the membrane became compacted.

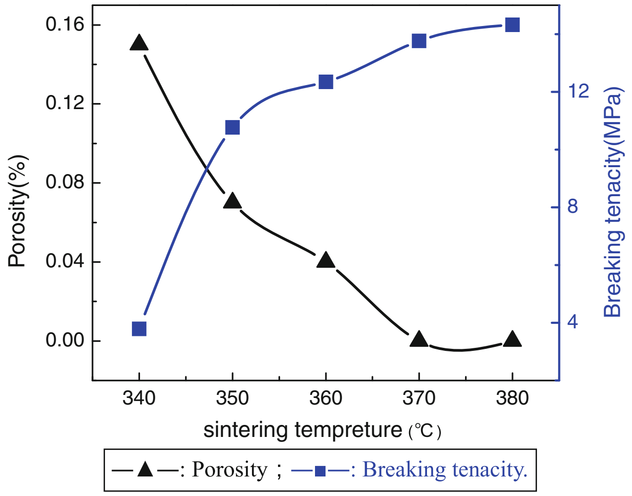

Fig. 5 The influence of sintering temperature on the properties of m-PTFE membranes

Sintering state

Figure 6 shows different morphologies of m-PTFE membranes by relax and fixed setting sintering. It revealed that the micropores among the fibrils net nodes in the membrane are loose after fixed setting sintering while the micropores are compact by relax setting one. PTFE resins form decentralized structure in PVA carrier during the sintering process; PTFE resins adhere with each other partially which forms the micropore structures. In addition, when the membrane sintering was at fixed setting state, the PTFE macromolecule slipped in the fixed direction which was easy to form the fibril pore structure in Fig. 6b, while membrane shrinks by relax setting state which formed compact structure, Fig. 6a.

Conclusions

A novel method of producing PTFE membrane was used in this article. The PTFE membranes were prepared through PTFE suspension with PVA as the membrane carrier. Sintering model was proposed, and results showed that it was better to produce pore structure for PTFE membrane at the first sintering stage; however, the membrane became compact with the increasing sintering temperature. The PTFE membranes obtained (m-PTFE) maintain both good thermal stability and strong hydrophobicity.

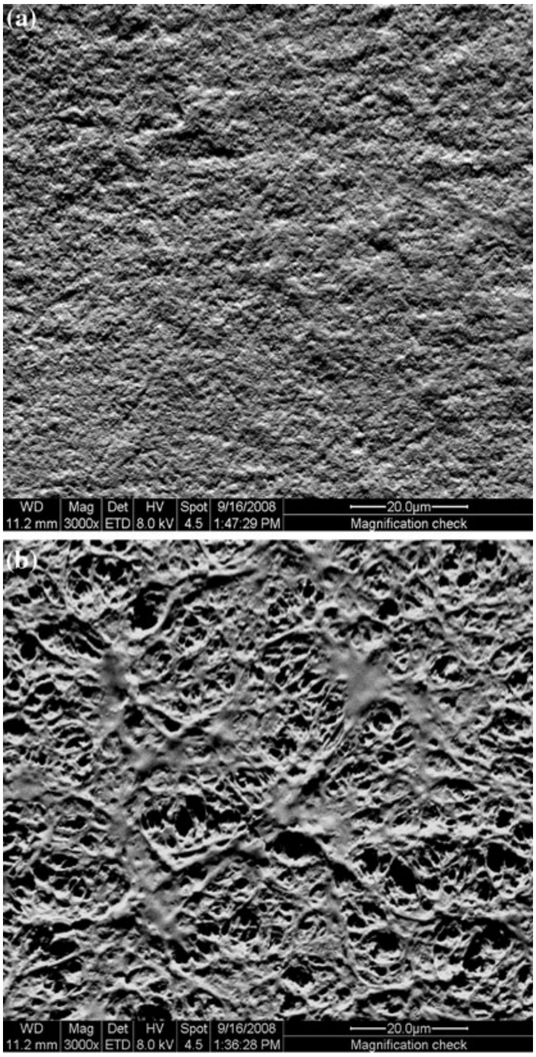

Fig. 6 SEM photographs of m-PTFE membranes by different sintering state. **a** relax setting, **b** fixed setting

Acknowledgements The author gratefully acknowledges the financial support of the national high technology research development plan of china: the key technology of producing polyolefin high performance microfiltration and ultrafiltration hollow fiber membrane ("863" fund program No. 2007AA030304), and the National Natural Science Foundation of China (Grant No. 51073120).

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