Preparation and Properties of Poly(tetrafluoroethylene)/Calcium Carbonate Hybrid Porous Membranes

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ABSTRACT: Poly(tetrafluoroethylene) (PTFE)/calcium carbonate ($CaCO_3$) hybrid porous membranes were prepared from a mixture of PTFE emulsion and nanoscale $CaCO_3$ particles by using polyvinyl alcohol as the fiber forming polymer. The interfacial microvoids (IFMs) were obtained owing to the different mechanical properties of PTFE and $CaCO_3$. Effects of $CaCO_3$ contents and membrane draw ratios on membranes structure and properties were investigated. Results showed that: (1) as the $CaCO_3$ content increase, the membrane hydrophobicity improved owing to the increasing of membranes surface roughness, (2) the membrane porosity and pure water flux increased as the $CaCO_3$ content and membrane draw ratios increasing. By the membrane morphology configuration with scanning electron microscopy, it was found that the IFMs quantity and pore size improved obviously with the draw ratios increasing. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: E116–E122, 2012

Key words: polytetrafluoroethylene; porous membrane; interfacial micro-voids; morphology

INTRODUCTION

Poly(tetrafluoroethylene) PTFE has many unique characteristics such as excellent chemical resistance, thermal stability, strong hydrophobicity, low surface friction, and high fracture toughness. These exceptional combination properties make PTFE the prime material for membrane applications, especially for industrial separation and membrane distillation.[1–4] However, the main disadvantage of PTFE is that its poor processing property prohibits common phase inversion or melt spinning methods from fabricating porous membrane.[5,6] Currently, the method[7–9] of fabricating PTFE porous membrane involves blending a nonsintered PTFE resin and liquid lubricant and then the blends are extruded at a high temperature. The extruded material is drawn by uniaxial or biaxial stretching and heat to about 327°C or above to form the PTFE resin porous membrane. However, these methods suffered from inferior performance of the product due to the pore controllability of the porous structure or inferior membrane-formability,

which results in an impractically large thickness of the product membrane.

Presently, many patents have disclosed the methods of producing high performance polyvinylidene difluoride (PVDF) hollow fiber membrane by introducing organic liquids and inorganic particles into PVDF matrix.[10,11] However, there are few researches focusing on PTFE hybrid porous membrane using inorganic particles. Additional, studies on the interfacial microvoids (IFMs) between PTFE and inorganic particles have not been reported so far. As a kind of inorganic additive, nanoscale calcium carbonate ($CaCO_3$) particle is widely used in the field of composite polymer, membrane fabrication, and so on.[12–14]

The objective of this article is to provide a novel method of producing PTFE porous membrane by introducing $CaCO_3$ particles into PTFE matrix. A series of PTFE/$CaCO_3$ hybrid membranes with different $CaCO_3$ contents were prepared, and effects of $CaCO_3$ contents and membrane draw ratios on membranes structure and properties were investigated in this article.

EXPERIMENTAL

Materials

PTFE emulsion is a commercial product (3F new materials, Shanghai) designed as FR301B, with characteristics shown in Table I; polyvinyl alcohol (PVA)

TABLE I
Characteristics of PTFE Emulsion

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

is purchased from Sanwei Group, Shanxi. Type:2488 (polymerization degree:2400; alcoholysis:88%). CaCO$_3$ particle powder is purchased from Shanghai Yaohua Nano-Tech. Average rang of particle size is 60–90 nm.

Membrane preparation

CaCO$_3$ particles were dried for 12 h at 100 ± 2°C in a vacuum oven (2 mbar) to remove the moisture content before use. Then CaCO$_3$ particles were dispersed homogenously in PTFE emulsion by ultrasonic vibration. PVA solution (mass ratio of PVA/H$_2$O = 1 : 4) was prepared by dissolving PVA powder in distilled water at 90°C under constant stirring for at least 6 h. When the solution cooled down to room temperature, the PTFE and CaCO$_3$ blends were added to PVA solution with constant stirring for 3 h to form a homogenous dope. The mass ratios of CaCO$_3$/PTFE were 0, 1/9, 2/8, and 3/7, respectively. After degassing for 8 h with a vacuum pump (2 mbar), the dope was then cast into film on a clean and smooth stainless steel plate. After sintering at 360°C, PTFE/CaCO$_3$ hybrid membranes were finally obtained. The membranes ID were shown in Table II. In addition, the hybrid membranes were drawn with draw ratios of 1.5, 2, and 2.5 in boiling water.
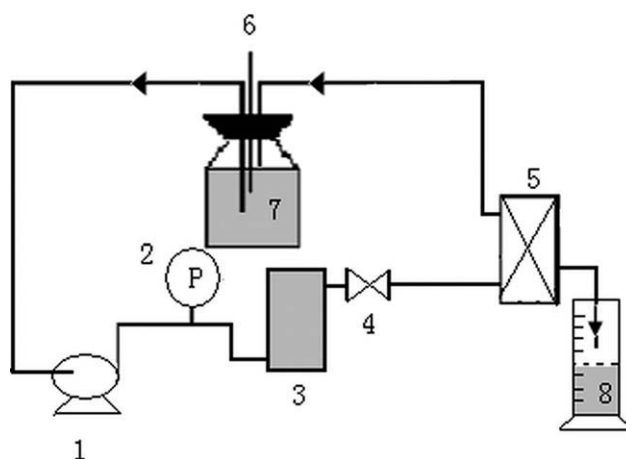
Method and measurements

PWF test

The pure water flux (PWF) of the membranes were determined by the following equation:

$$J = V/(A \times t) \tag{1}$$

TABLE II
**PTFE Hybrid Membranes with Different CaCO$_3$ Contents**

	Membrane ID			
	PTFE	Hybrid-1	Hybrid-2	Hybrid-3
CaCO$_3$/PTFE mass ratio	0	1/9	2/8	3/7
Dope viscosity (Pa s)	0.85	1.15	2.55	3.21

Figure 1 The schematic diagram of water flux test setup. (1) peristaltic pump, (2) pressure gauge, (3) the buffer bottle, (4) valve, (5)flat-sheet membrane, (6) thermometer, (7) feed tank, and (8) permeation.
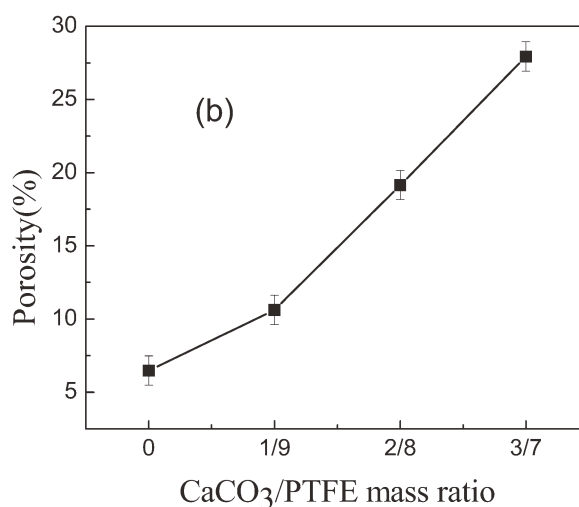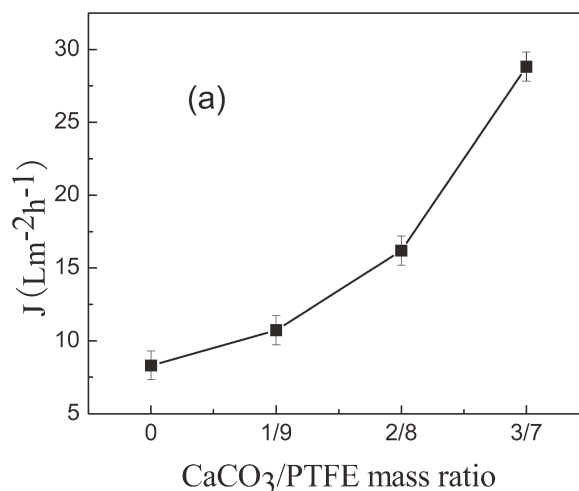
Figure 2 Effects of CaCO$_3$/PTFE mass ratio on the PWF and porosity of membranes. (a) PWF and (b) porosity (working pressure was 0.1 MPa).
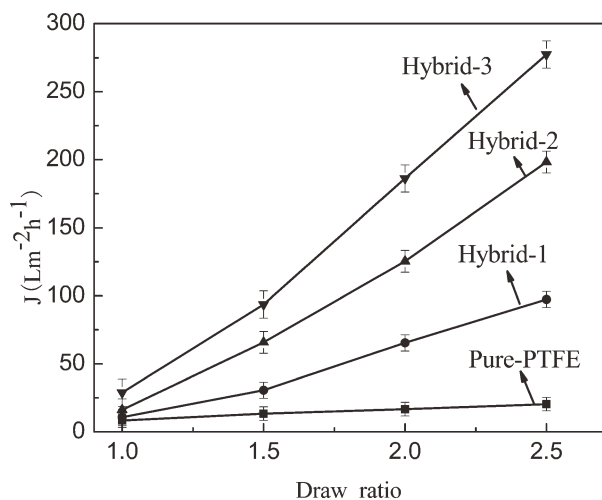
Figure 3 Effect of draw ratio on PWF of hybrid membranes.

where J is PWF ($Lm^{-2} h^{-1}$), V is the total of permeation (L), A is the membrane area (m^2), and t is sampling time (h). The PWF measurement apparatus was shown in Figure 1.

Contact angle

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

Dynamic mechanical analysis

Dynamic mechanical properties were evaluated via dynamic mechanical analysis (DMA; NETZSCH, DMA 242C). It was investigated under N_2 atmos-

phere and the thermal program was set at a heating rate of 10 °C min^{-1} from 0 to 400°C

Porosity

The porosity was determined by gravimetric method,[15] which measured the weight of liquid contained in the membrane pores. Because of the hydrophobicity of PTFE, isopentane was used as the wetting liquid. Formula (2) was used to calculate ε of the membrane,

$$\varepsilon = \frac{(w_1 - w_2)/D_1}{(w_1 - w_2)/D_1 + w_2/D_p} \qquad (2)$$

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 apparent density of PTFE and CaCO$_3$ calculated through the percentage of CaCO$_3$ particles in PTFE matrix ($D_{PTFE} = 2.20$ g cm^{-3}, apparent density of CaCO$_3$, $D_{CaCO3} = 0.4$ g cm^{-3}).

Scanning electron microscopy

Morphologies of membrane samples were examined using scanning electron microscopy (SEM, FEI, Quanta200, The Netherlands). 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.

RESULTS AND DISCUSSION

Pure water flux

As it is known, PTFE membrane porosity is relatively low by sintering method. Moreover, the sintering pore is impermeable and the pore size is limited by the size of PTFE resin. Therefore, it is meaningful to explore a novel method to improve the PTFE membrane porosity. As for PTFE/CaCO$_3$ hybrid membrane, the porosity was composed of two parts: one was the sintering pore structure and the other was the IFMs structure formed between PTFE matrix and CaCO$_3$ particles.

Figure 2 showed the PWF and porosity of hybrid membranes with different CaCO$_3$ contents. It can be clearly seen that the PWF was improved with the

TABLE III
Effect of Draw Ratio on Membrane Thickness and Maximum Pore Size

Membrane ID	PTFE				Hybrid-1				Hybrid-2				Hybrid-3			
Draw ratio	1	1.5	2	2.5	1	1.5	2	2.5	1	1.5	2	2.5	1	1.5	2	2.5
Max pore size (µm)	0.23	0.23	0.25	0.27	0.32	1.51	2.73	5.32	0.57	4.32	5.14	6.03	0.62	4.23	5.88	7.64
Thickness (µm)	43.7	38.2	36.1	33.5	47.4	45.2	43.6	40.8	48.2	46.1	43.9	41.2	47.2	45.6	42.8	41.1
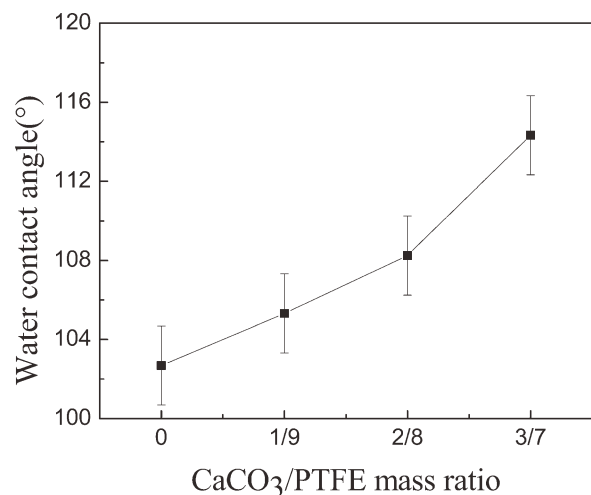
Figure 4 Effect of CaCO₃ amount on the water contact angle of hybrid membranes.

increasing of CaCO₃ contents. When the CaCO₃/PTFE mass ratio was zero, there were only sintering pore structures in the membrane, which induced the PWF and porosity very low. As for PTFE hybrid membranes, the CaCO₃ particles were dispersed in the PTFE matrix. Owing to the low surface energy of PTFE, PTFE and CaCO₃ were incompatible, which induces the formation of IFMs between PTFE and CaCO₃. Comparing with PTFE membrane, there were not only sintering pore structures but also the IFMs in hybrid membranes. As the CaCO₃ contents increasing, the IFMs quantity increased which inducing the promotion of PWF and porosity.

Effects of draw ratios on PWF of PTFE membrane and hybrid membranes were shown in Figure 3. As it is known, the mature method producing PTFE porous membrane is biaxial stretching method to get the node-fibril pore structure.[16–18] However, this method requires PTFE relatively high crystallinity and appropriate drawing condition. The node-fibril network is formed during the biaxial stretching process, while the aim of the drawing process in this article is producing the IFMs. As for PTFE membrane, there were no obvious changes in PWF with the increasing of draw ratios. When CaCO₃ were introduced into PTFE matrix, there were interfacial separation occurred between PTFE and CaCO₃ after stretching which induced the promotion of the membrane PWF. This may be attributed to different reasons, for example, PTFE was easier to deform when the hybrid membranes were stretched nearby the glass transition temperature (T_g). During the stretching process, the IFMs were formed because of the mechanical deformation difference of polymer matrix and inorganic particles. Under the same draw ratio, the IFMs quantity increased obviously with the increasing of CaCO₃ contents. This tendency can be ascribed to two main factors: one was that more

and more new IFMs created as the draw ratio increased. The other one was that the interface separation between PTFE and CaCO₃ aggravated, which induced the enlargement of IFMs pore diameter. In addition, the decrease of membrane thickness led to the promotion of PWF. The thickness and the maximum pore size of membranes were shown in Table III.

Hydrophobicity

Hydrophobicity is an important property that makes PTFE widely be used in the field of waterproof and breathable, membrane distillation.[2,9–20] It is meaningful to keep the strong hydrophobicity during the manufacture process. Currently, many efforts have been made on the researches concerning on the surface structure, which significantly influence the hydrophilic property. It is well known, not only the material chemical constitution but also the surface structure determine the hydrophilic property. Furthermore, the surface structure includes surface roughness and porosity.[21–23]

Wenzel[24] has made deep researches about the effect of surface roughness on the membrane hydrophobicity. Moreover, the Young's equation has been corrected. It indicates that the actual contacting area is bigger than ideal plane and Wenzel equation is proposed:

TABLE IV
Comparison on Water Contact Angles of PTFE and Hybrid-1 Membranes After Stretching

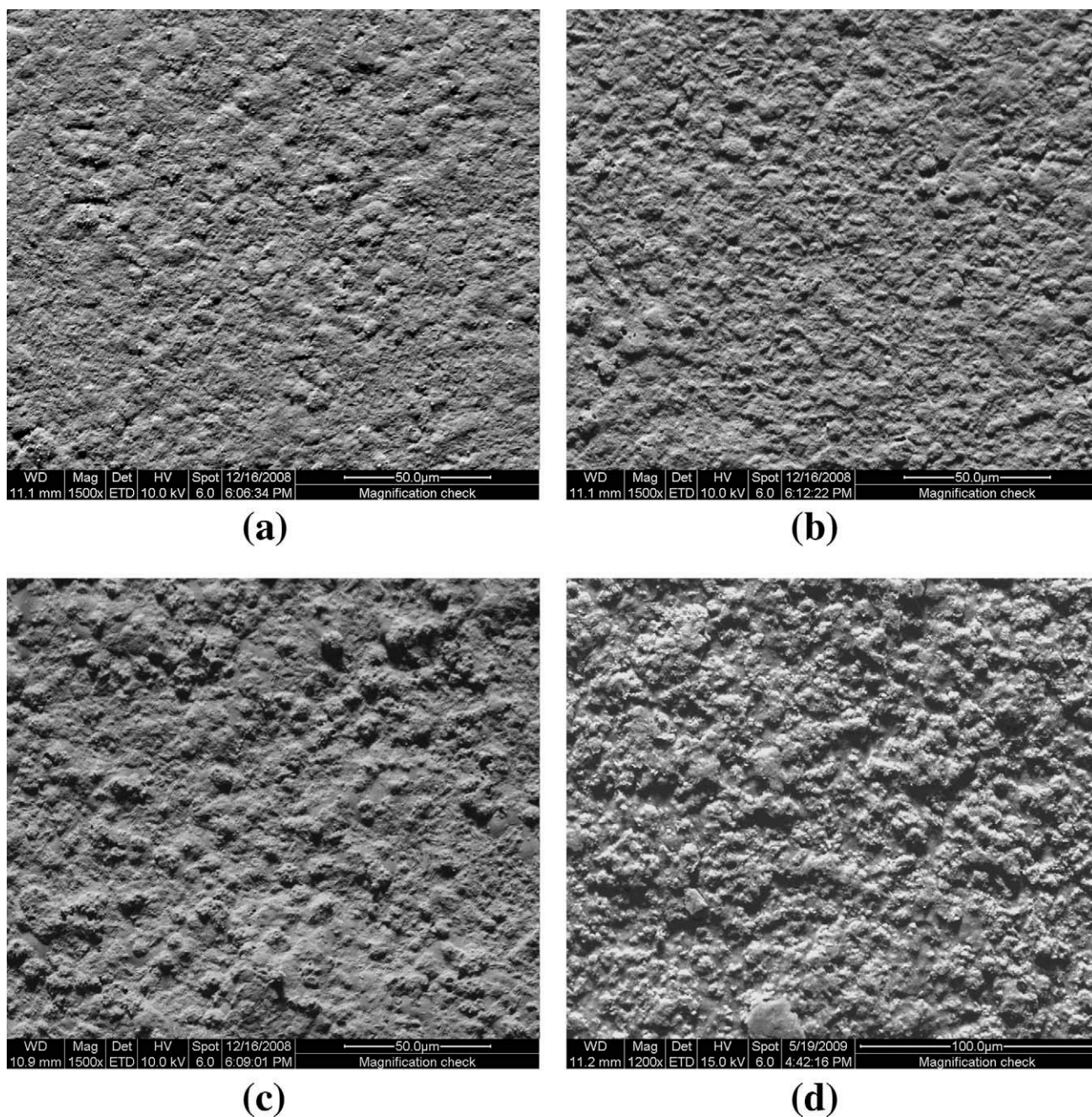| Drawn times Membrane ID	1	2	3
PTFE	101.31 ± 2°	102.51 ± 2°	102.26 ± 2°
Hybrid-1	105.84 ± 2°	110.62 ± 2°	118.18 ± 2°
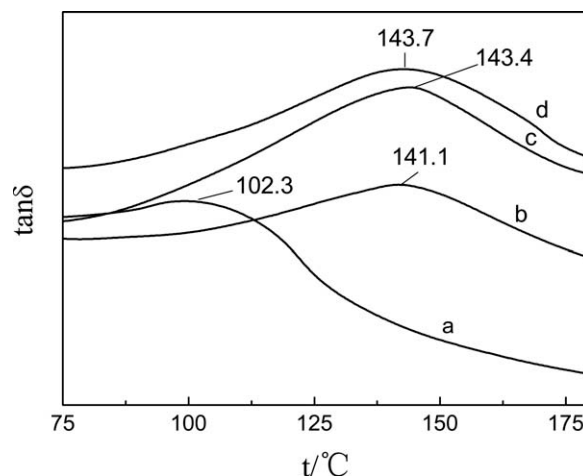
Figure 5 The DMA diagram of hybrid membranes with different CaCO₃ contents. (a) PTFE, (b) hybrid 1, (c) hybrid 2, and (d) hybrid 3.
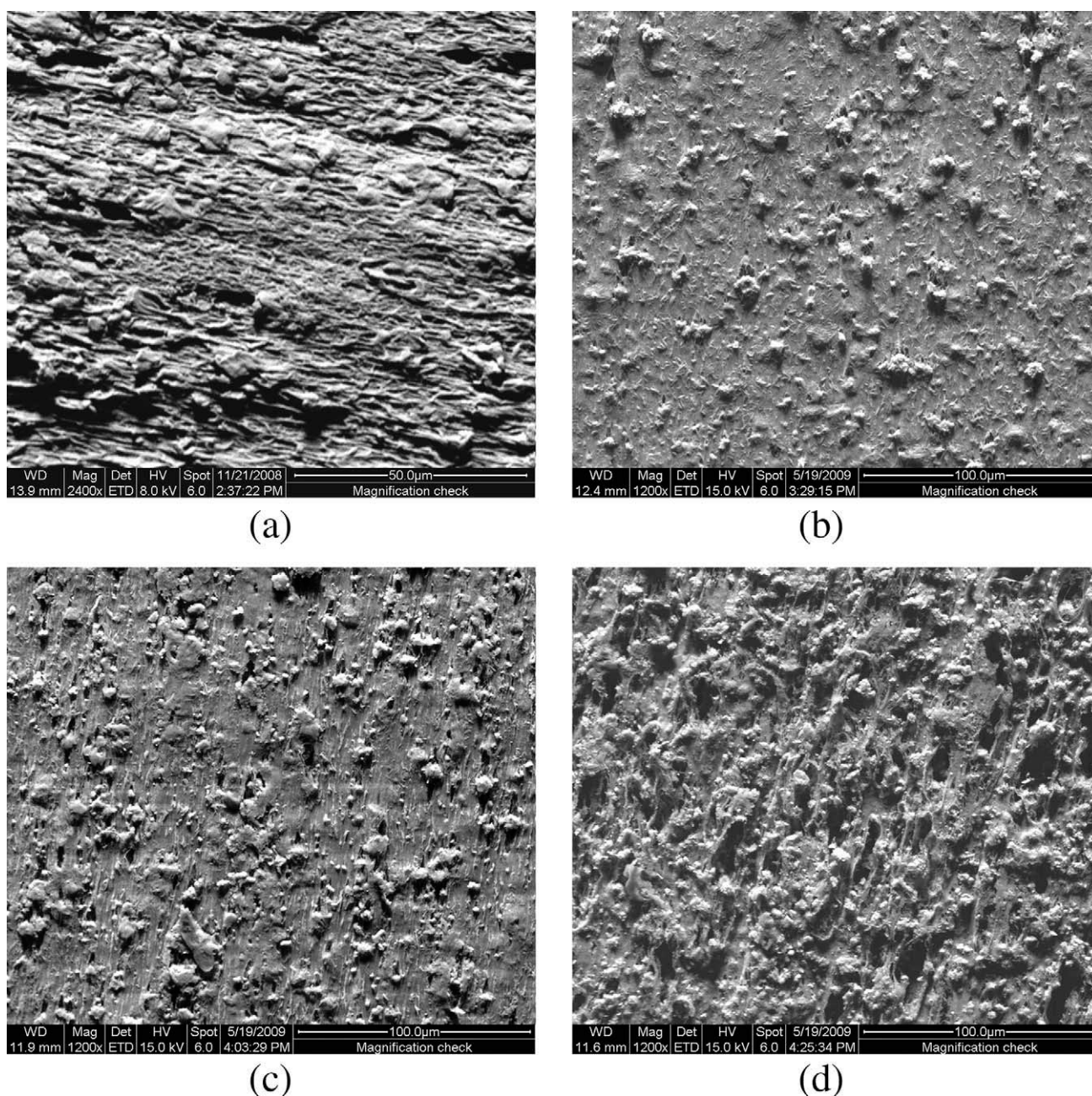
Figure 6 SEM pictures of surface morphology of PTFE and hybrid membranes. (a) PTFE, (b) hybrid 1; (c) hybrid 2, and (d) hybrid 3.

$$\cos \theta' = r(\gamma_{sv} - \gamma_{sl})/\gamma_{lv} \qquad (3)$$

where r is the quotient value of actual and apparent contacting area. Comparing with Young's equation, $\cos \theta' = r \cos \theta$, θ' is apparent contact angle, θ is Young's contact angle. It is obvious that $r > 1$. Through Wenzel equation, we can know that as the roughness of membrane increasing, hydrophilic membrane will be more hydrophilic while hydrophobic membrane will be more hydrophobic.

Figure 4 illustrated that the water contact angles of hybrid membranes rose as the $CaCO_3$ contents increasing. It is well known, PTFE is the most hydrophobic polymer because of its low surface energy. Moreover, the membrane surface roughness improved with $CaCO_3$ contents increasing. According to Wenzel equation, the water contact angles rose with the hybrid membranes surface roughness increasing. Results shown in Table IV also demonstrated the same conclusion. The water contact angles of PTFE and PTFE/$CaCO_3$ hybrid membranes

Figure 7 Comparisons of surface morphology of PTFE and hybrid membranes after stretching. (a) PTFE × 2.5 draw ratio, (b) hybrid 2 × 2 draw ratio; (c) hybrid 2 × 2.5 draw ratio; (d) hybrid 3 × 2.5 draw ratio.

after stretching were tested. From the results, there were no obvious changes in the water contact angle of PTFE membrane with different draw ratios. This may be due to little differences on the membranes surface roughness although the membranes were stretched. However, the hybrid membranes showed the opposite results. The PWF of hybrid membranes improved with increasing draw ratios (seen in Fig. 3). The surface roughness of hybrid membranes was promoted with increasing drawn ratios, which enhanced the hydrophobicity of hybrid membranes.

Thermal properties

DMA is used to investigate the interfacial adherence between polymer matrix and the inorganic particle.[25] Rigid inorganic filler significantly influence the modulus and glass transition temperature (T_g) of the polymer.

Figure 5 showed the temperature-loss curves of PTFE and hybrid membranes. In DMA spectra, the temperature corresponding to α peak was the glass transition temperature (T_g). The introduction of CaCO$_3$ made T_g move from about 100°C to nearby 140°C. It was because that CaCO$_3$

particles limited the movement of PTFE molecular chains, which made the glass transition more difficult.

Morphologies

The SEM pictures (Figure 6) showed the surface morphologies of PTFE and hybrid membranes. The surface of PTFE membrane was remarkably smooth, while the hybrid ones were rough. Furthermore, increasing of $CaCO_3$ contents improved the hybrid membranes roughness degree. As for PTFE membrane, PTFE resins formed decentralized structure in PVA matrix before sintering process. Then PVA was removed by sintering; meanwhile, PTFE resin melt and adhered with each other forming compact and smooth surface [Fig. 6(a)]. Thus, the analysis agreed with the low PWF of PTFE membrane investigated above.

Figure 7 illustrated the obvious differences on the surface morphologies of PTFE membrane and hybrid membranes after stretching. PTFE resins formed compact structure during the sintering processing. There was no pore created when PTFE membrane were drawn up to the ratio of 2.5 [Fig. 7(a)]. Figure 7(b) showed the surface morphology of hybrid-2 membrane drawing two times. The IFMs were created owing to the interface separation between $CaCO_3$ and PTFE. Furthermore, the IFMs quantity and size improved with draw ratios increasing [Fig. 7(c)]. As for Figure 7 (d), the quantity and size of IFMs obviously improved comparing with Figure 7(c). It was because that the interface quantity increased as $CaCO_3$ contents rose from 2/8 to 3/7. Therefore, introduction of $CaCO_3$ into PTFE matrix was aid to produce IFMs by properly stretching. In addition, the IFMs structure was completely different from the node-fiber network produced by biaxial stretching method.

CONCLUSIONS

$PTFE/CaCO_3$ hybrid porous membranes were prepared from a mixture of PTFE emulsion and nanoscale $CaCO_3$ particles by using PVA as the fiber forming polymer. The IFMs were created when the hybrid membrane suffered stretching. Moreover, the membrane hydrophobicity improved owing to the increasing of membranes surface roughness. The membrane porosity and PWF increased as the $CaCO_3$ content and membrane draw ratios increasing.

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