Preparation and Properties of Polytetrafluoroethylene/CaCO₃ Hybrid Hollow Fiber Membranes

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ABSTRACT: A novel method of preparing polytetrafluoroethylene (PTFE) hollow fiber membrane was presented by utilizing poly (vinyl alcohol) (PVA) can form a gel of two dimensional complex compounds with Boric acid (H_3BO_3). Effects of H_3BO_3 on PTFE nascent hollow fiber were investigated, and the results showed that the introduction of H_3BO_3 effectively reduced the addition of PVA. The configuration named "fibril" formed between PVA and H_3BO_3 could be observed in nascent hollow fiber by SEM (Scanning electronic microscopy). Furthermore, Calcium carbonate ($CaCO_3$) particles (60 nm~90 nm) were introduced into PTFE matrix. The interfacial microvoids (IFMs) which were different from the PTFE sintering or node-fibril network structure were obtained. The assumption of the IFMs formation was proposed in this study. Effects of $CaCO_3$ amount and draw ratios on structure and properties of hybrid hollow fiber membranes were analyzed, and the SEM results showed that the IFMs quantity and diameter improved with draw ratio increasing. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 324–330, 2012

Key words: PTFE; membranes; morphology; fiber-forming; $CaCO_3$ particles; IFMs

INTRODUCTION

Polytetrafluoroethylene (PTFE) is a desirable filtration membrane material because its excellent chemical and thermal stability are widely used in the field of industrial filters, membrane distillation.[1–3] However, PTFE's inherent inert nature renders that it is impossible to be cast into membrane by conventional solution immersion casting process, and also to be spun into hollow fiber membrane by melt-spinning method.[4–7]

Commercially, all available PTFE hollow fiber membranes are referred as "hollow tubes,"[8] probably because they have relatively larger size than normal hollow fiber membrane. Manufacturing processes for making PTFE hollow tube involves extruding PTFE paste into tubular shape, sintering the tube into PTFE solid tube after the lubricants are extracted, and finally stretched longitudinally to make porous. The Sumitomo in Japan does the outstanding works on PTFE hollow fiber membrane.

The product Poreflon® has the average pore size of 0.45 μm, and mechanical strength can reach 80N. Comparing with typical PTFE sheet membrane produced by biaxial stretching method, the pores in this tube are only "half formed," and they do not attain the "node to fibril network."

Currently, there are many researches on producing PTFE fiber with Poly(vinyl alcohol) (PVA) or Viscose as fiber-forming polymer through emulsion spinning technology.[9–12] Emulsion spinning technology involves spinning nascent fiber from mixture solution of PTFE dispersion and fiber-forming polymer, after which the fiber-forming polymer are removed by sintering process, and finally the PTFE fiber is obtained.

However, few reports could be seen about PTFE membrane preparation by PTFE emulsion. Takashi Kawai[13] in Japan provided a method in which blending PTFE emulsion and sodium alginate to get spinning dope. The spinning dope was then spun into hollow fiber by conventional dry-wet spinning method. Subsequently, the PTFE hollow fiber membrane was finally obtained after the sodium alginate removed by sintering. However, this method requires large amount of fiber-forming polymer as to promote the spinning dope viscosity. So it needs more time and energy to remove the fiber-forming polymer in the following sintering processes. Xiong[14] in china prepared spinning solution by blending PVA and PTFE emulsion with different

TABLE I
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.

mass concentrations. Then the spinning dope was electrospun into composite nanofibers, whereby the PTFE porous membranes were obtained after sintering.

Interfacial microvoids (IFMs) as a novel membrane pore have now been an attractive field and several such membranes have been studied by polymer/polymer blending or polymer/inorganic hybrid. Hu[15] has studied the relationship between the composition of the PVDF/PU blend membranes and their IFMs. Li[16] has prepared PU/SiO$_2$ hybrid membrane and studied the formation of the IFMs. However, researches on PTFE blend membranes are relatively few and studies on the IFMs are also so far unreported.

Nano-Calcium carbonate (CaCO$_3$) is a usual material being widely applied in inorganic particle-filled PTFE composites. The surface modified CaCO$_3$ particles which had been coated with organic film would well dispersed in PTFE matrix.[17,18]

This article aims to provide a novel method to produce PTFE hollow fiber membrane based on the emulsion spinning technology. We used the gel of PVA/H$_3$BO$_3$ as the fiber-forming carrier and introduced CaCO$_3$ particles into PTFE matrix to produce PTFE hybrid hollow fiber membranes. A kind of pore structure named IFMs was obtained between PTFE matrix and CaCO$_3$ particles after the hollow fiber membrane stretching. Meanwhile, IFMs were different from the PTFE node-fibril network produced by biaxial stretching process.

EXPERIMENTAL

Materials

The PTFE concentrated suspension is a commercial product (3F new materials, Shanghai) designed as FR301B, with characteristics shown in Table I. Polyvinyl alcohol (PVA) was purchased from Sanwei Group, Shanxi, China. Type: 2488 (polymerization degree: 2400; alcoholysis: 88%). Calcium carbonate (CaCO$_3$) particle powder, purchased from Shanghai Yaohua Nano-Tech, Shanghai, China. Average rang of particle size is 60–90 nm. Boric acid (H$_3$BO$_3$) and sodium sulphate (Na$_2$SO$_4$), analytical reagent, purchased from Tianjin Kermel Chemical Reagent, Tianjin, China.

Preparation of PTFE hollow fiber membranes

CaCO$_3$ particles were dried for 12 h at 100 $\pm$ 2°C in a vacuum oven (2-m bar) to remove the moisture content before use. Then CaCO$_3$ particles were dispersed homogenously in PTFE suspension by ultrasonic vibration. Meantime, homogeneous PVA aqueous gel solution was obtained after PVA resins and H$_3$BO$_3$ were swelled in distilled water at 40°C and were stirred at 70°C for 1 h (mass ratio of PVA/H$_2$O = 1 : 9, H$_3$BO$_3$ addition loading in PVA was 3%wt). Then, PTFE suspension with CaCO$_3$ particles were added into the formulated solution. Kept stirring until PTFE and CaCO$_3$ particles were dispersed homogenously, then the solution was fabricated into hollow fiber by dry-jet wet spinning processes after degassing for half-a-day. The dope container was connected with a N$_2$ gas cylinder. Basically, the dope was dispensed under pressure through a selfmade hollow shape spinneret at a controlled rate and went through an air gap before immersing into the coagulation bath. A mixture of NaOH/Na$_2$SO$_4$/water was used as the bore fluid while ethanol was utilized as external coagulant. Then the PTFE nascent hollow fibers were

TABLE II
Spinning Parameters of Hollow Fibers with Different Proportion

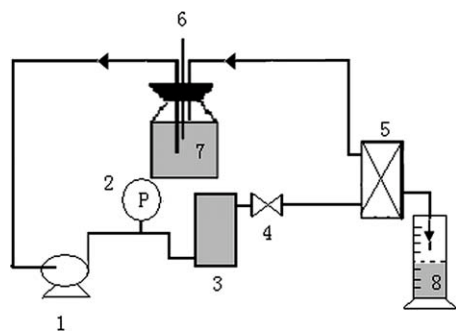|	Hollow fiber ID			
Nascent hollow fiber	Nascent-0	Nascent-1	Nascent-2	Nascent-3
Dope composition	PTFE/PVA: 90/10 (solid content), H$_3$BO$_3$ loading in PVA was 3 wt %			
CaCO$_3$ loading in PTFE addition	0	5%	10%	20%
Dope temperature (°C)	70			
Bore fluid (wt%)	NaOH/Na$_2$SO$_4$/water: 5/25/70			
Extra coagulation	Ethanol			
Bore fluid temperature (°C)	25 $\pm$ 1			
Air gap(cm)	3			
After sintering	Hybrid-0	Hybrid-1	Hybrid-2	Hybrid-3
Sintering temperature (°C)	360°C			
Sintering time (min)	5 min			
Sintering state	Relax state			

Figure 1 The schematic diagram of water flux test setup. (1) peristaltic pump, (2) pressure gauge, (3) the buffer bottle, (4) valve, (5) hollow fiber membrane, (6) thermometer, (7) feed tank, and (8) permeation.

obtained. After sintering at 360°C to remove the film-forming polymer PVA, CaCO$_3$ hybrid PTFE hollow fiber membranes were finally obtained. In addition, the hollow fiber membranes were drawn with draw ratios of 1.5, 2, and 2.5 in boiling water for 15 min. The hollow fiber samples were tabulated in Table II.

Characterization

Viscosity of the spinning solution was test by NDJ-7 rotary viscometer (Shanghai Balance Instrument Company). The steady-state shear viscosity was measured by a 25-mm cone-plate fixture at 70°C, and the shear rate is 350 S^{-1}.

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.

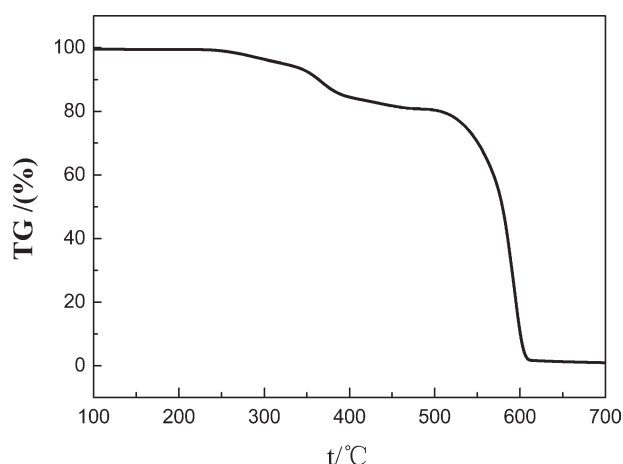The pure water flux (PWF) of the hollow fiber membranes were determined by the following equation[19]

Figure 3 Gel mechanism of PVA and H$_3$BO$_3$.

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

where J is PWF (L m^{-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. Since the PTFE's hydrophobicity, the membrane was immersed in the alcohol prior the PWF test.

The bubble point pore diameter was measured by using the gas permeation method using capillary flow porosimetry system (CFP-1100-A*, America Porous Materials corporation). The bubble point pore diameter can be defined as Laplace equation[20]:

$$r = \frac{2\sigma \cos \theta}{\Delta p} \tag{2}$$

where σ is the coefficient of surface tension of the wetting fluid, θ is the contact angle between wetting fluid and membrane, Δp is the operating pressure when the first bubble appears.

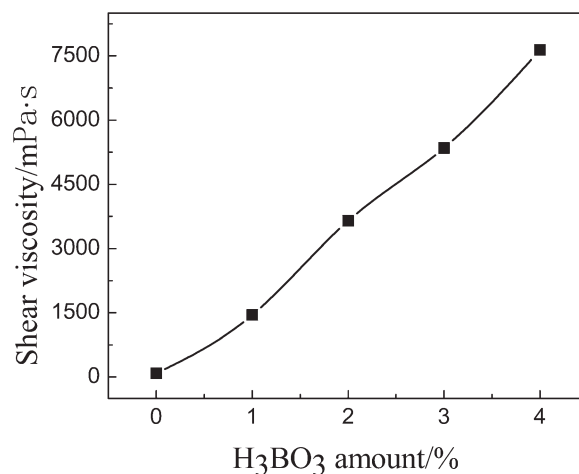The morphology of the resulting hollow fiber membranes was examined by scanning electron microscopy

Figure 2 TGA curve of the PTFE/PVA nascent hollow fiber.

Figure 4 Effect of H$_3$BO$_3$ on the shear viscosity of spinning solutio.

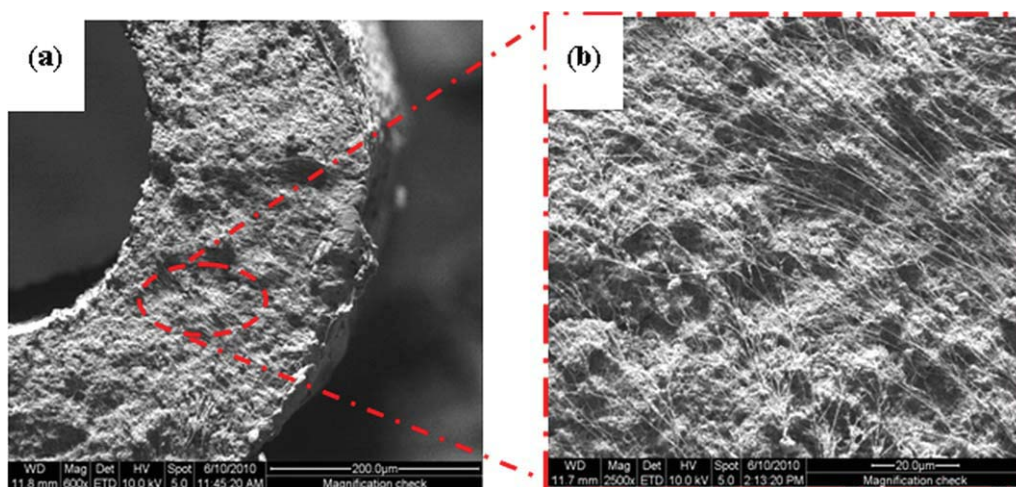**Figure 5** SEM photographs of cross section morphology of Nascent-0. (a) ×600, (b) ×2500. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(SEM, FEI, Quanta 200, Netherlands). Hollow fiber membranes were frozen in liquid nitrogen followed by fracturing to expose the cross-sectional areas. Samples were gold coated and viewed with SEM.

RESULTS AND DISCUSSION

Determination of the sintering temperature

The sintering temperature was determined by the TGA data. The TGA curve obtained by thermogravimetric analyzer was shown in Figure 2. It could be seen that the weight loss was located at 300–400, which corresponded to trace of PVA while the decomposition of PTFE began at 500°C. In the range of 400–500°C, there was no weight change. This meant that PTFE was preserved well and PVA decomposed completely. So in this study, the sintering temperature of 360°C was chosen.

Effects of H_3BO_3 on PTFE nascent hollow fiber

Gel mechanism of PVA and H_3BO_3

The conventional method which was wet-spinning process involved blending PVA solution and H_3BO_3 to get the spinning dope.[21] The —OH in PVA can react with the —H in H_3BO_3, which can form a kind
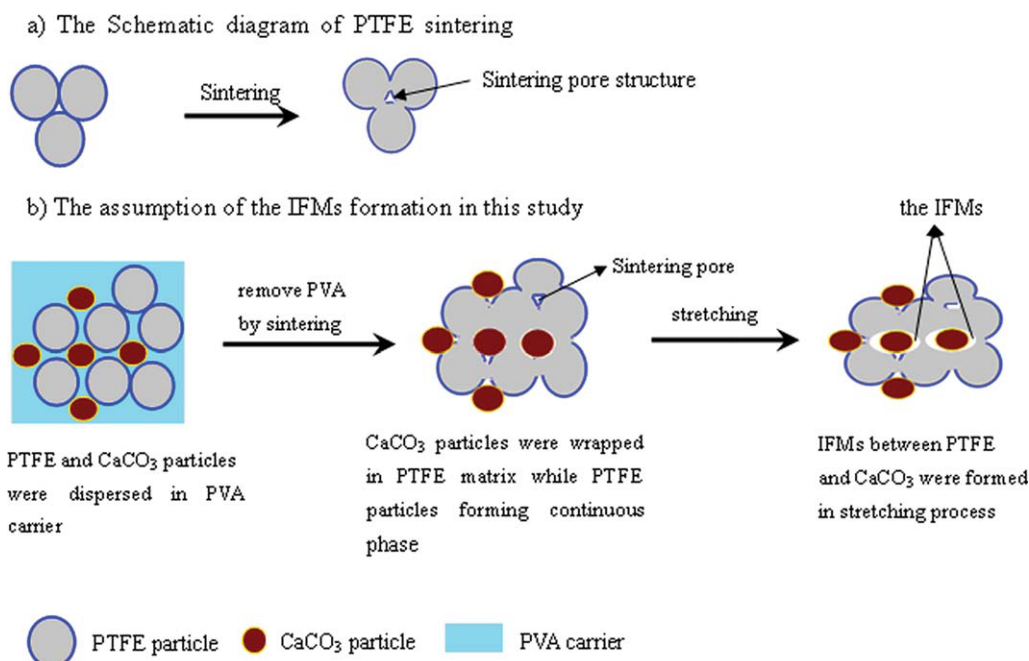

Figure 6 The proposed pore structure formation of PTFE/CaCO$_3$ hybrid hollow fiber membrane. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
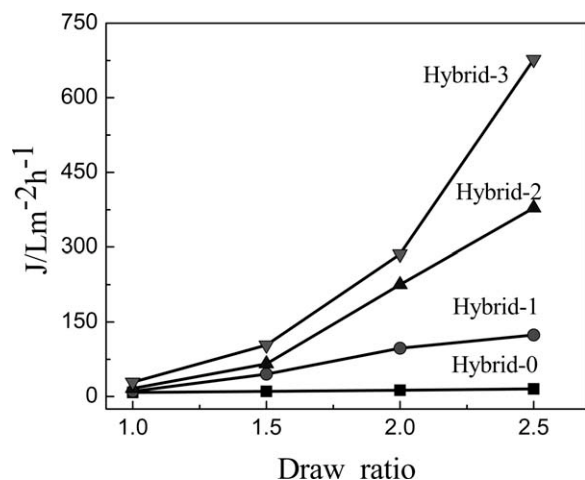
Figure 7 Effect of draw ratio on PWF of hybrid hollow fiber membranes.

of two-dimensional complex compounds.[22] The shear viscosity increased because of the complex formation between PVA chains. The gel mechanism of PVA and H_3BO_3 was shown in Figure 3. Therefore, the dope spinnability was enhanced even if less PVA amount was added. The viscosity of the spinning dope can be regulated by changing the addition of H_3BO_3. The solid composition was PTFE/PVA with mass ratio 90/10. The results were shown in Figure 4, it could be seen that the shear viscosity promoted with the increasing H_3BO_3 amount. The shear viscosity according to 3 wt % was 5350 mPa s, which met the spinning requirement well. So 3 wt % was adopted as the H_3BO_3 amount in the spinning dope proportion.

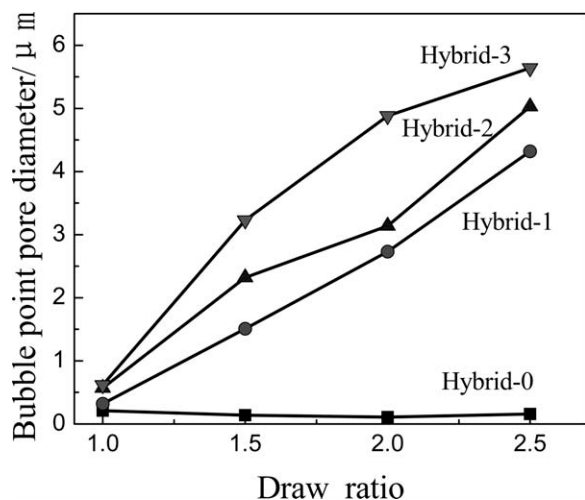Morphologies of nascent PTFE hollow fiber

Figure 8 Effect of draw ratio on the bubble point pore diameter of hybrid hollow fiber membranes.
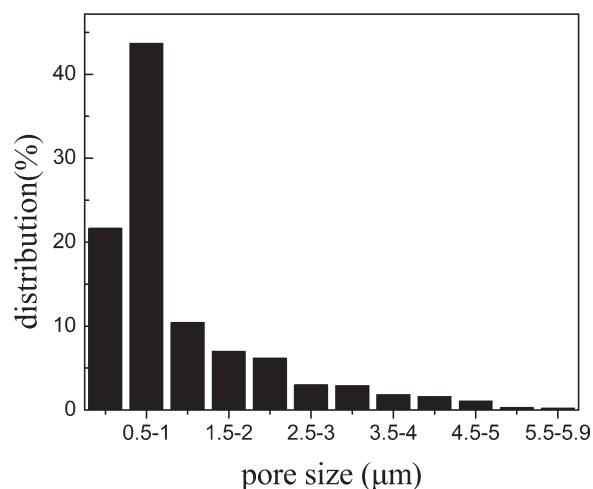
Figure 9 The pore size distribution of the hybrid-3 membrane after stretching.

An unusual configuration namely "fibril" was observed in the hollow fiber Nascent-0, as shown in Figure 5. The "fibril" structure was owing to the two-dimensional complex compounds formed between PVA and H_3BO_3 which promoted the shear viscosity of the PTFE/PVA spinning dope. In addition, obviously there was no pore structure in the nascent hollow fiber. Moreover, PTFE particles were dispersed homogenously in PVA continuous phase.

Effects of $CaCO_3$ on PTFE/$CaCO_3$ hybrid hollow fiber membrane

Formation of sintering pore structure and IMFs

The proposed pore structure formation of PTFE hybrid hollow fiber membrane in this study was shown in Figure 6. Figure 6(a) illustrated the pore formation of PTFE membrane by sintering method. As it is known, the porosity of PTFE membrane produced by this method was always relatively low, the pore structure was impermeable, and also the pore size was limited by the size of PTFE resin.

The assumption of the IFMs formation of PTFE hybrid hollow fiber membrane in this study was shown in Figure 6(b). In nascent hybrid hollow fiber, the PTFE and $CaCO_3$ particles dispersed homogeneously in PVA carrier. PTFE and $CaCO_3$ were dispersing phase while PVA was the continuous phase. During the sintering process, PTFE particles adhered with each other and formed the continuous phase, whereas PVA was removed by sintering. Besides, the interspaces between PTFE particles also formed the pore structure. In the process, $CaCO_3$ particle being the dispersing phase was wrapped in the PTFE matrix. However, the following stretching process made significant effects on IFMs formation. When the hybrid hollow fiber membrane was stretched nearly the glass transition temperature
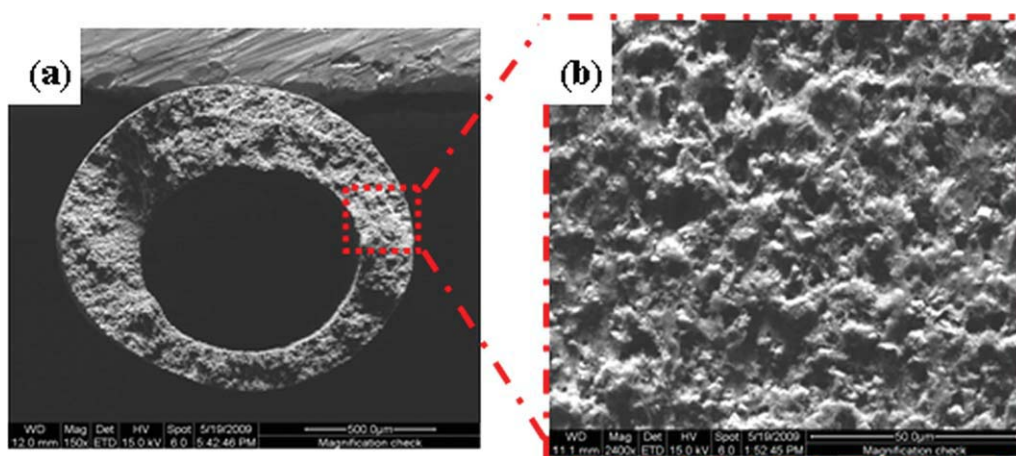
Figure 10 The cross-sectional morphologies of Hybrid-0. (a) 150×, (b) 2400×. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(T_g), the matrix PTFE was easier to be deformed, while $CaCO_3$ particles were rigid, thus the IFMs were formed. Furthermore, the porosity of the hollow fiber membrane depends on the quantity as well as the size of the IFMs which were influenced by the amount of $CaCO_3$ and the hollow fiber membrane drawn ratio.

Permeability of PTFE/CaCO$_3$ hybrid hollow fiber membranes

According to the assumption in 3.3.1, the PWF tests were used to measure the permeation properties of hybrid fiber membranes. Figure 7 showed the effects of draw ratio on PWF of hybrid hollow fiber membranes.
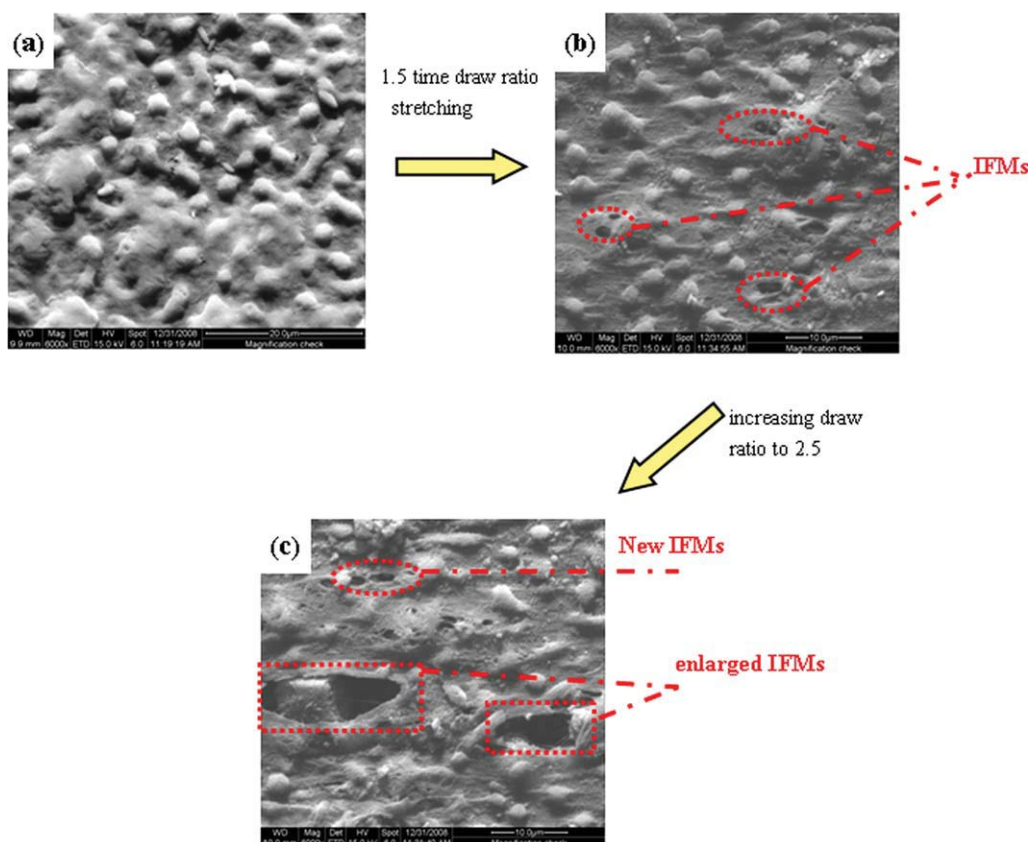

Figure 11 The IMFs formation of Hybrid-1 hollow fiber membrane changed with the increasing draw ratio stretch. (a) Hybrid-1-0; (b) Hybrid-1-1.5; (c) Hybrid-1-2.5, the number followed Hybrid-1 represented the draw ratio. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

As for hybrid-0 hollow fiber membrane, there were no obvious changes in PWF with draw ratio increasing. When $CaCO_3$ was added into PTFE matrix, the hybrid membrane PWF was improved significantly after stretching. With $CaCO_3$ amounts increasing, the IFMs quantity increased obviously after stretching by the same draw ratio. Meanwhile, as for hybrid-2 hollow fiber membrane, the increased degree was obviously higher with draw ratio increasing. This tendency can be ascribed to two main factors: the first one was that more and more new IFMs were created with the rising of draw ratio; the second one was that the interface separation between PTFE and $CaCO_3$ aggravated which induced the size of IFMs enlarging. In addition, the thickness of the hybrid membranes decreased with the increase in draw ratios, which would be helpful to the PWF promotion.

The bubble point pore diameter was used to measure the maximum pore size of hybrid hollow fiber membrane. Figure 8 illustrated the effect of draw ratios on the bubble point pore diameter of hybrid hollow fiber membranes. It obviously showed that the pore diameter improved with the increasing draw ratios on hybrid hollow fiber membrane. The results were consistent to the assumption pore structure formation of hybrid hollow fiber membrane shown in Figure 6. Moreover, the pore size distribution of the hybrid-3 after stretching is showed in Figure 9.

Morphologies of PTFE/$CaCO_3$ hybrid hollow fiber membranes

Figure 10 showed the cross section morphologies of Hybrid-0 hollow fiber membrane. The membrane obtained was a kind of homogeneous membrane. No finger-like pore structure was obtained as phase inversion method. Comparing with nascent hollow fiber, the "fibril" structure disappeared after sintering.

Figure 11 illustrated the IMFs formation of Hybrid-1 hollow fiber membrane changed with stretch draw ratio increasing. As shown in Figure 11(a), $CaCO_3$ particles were wrapped in PTFE matrix, and there was no obvious pore structure. When membrane was stretched, IFMs appeared [Fig. 11(b)]. With draw ratio increasing, the exiting IFMs diameter enlarged obviously owing to the aggrava-

tion of interface separation between PTFE and $CaCO_3$. In additional, there were many new IFMs appeared [Fig. 11(c)]. Thus, the results were agreed with the PWF test and the assumption formation of hybrid hollow fiber membrane.

CONCLUSIONS

PTFE/$CaCO_3$ hybrid hollow fiber membranes were prepared through PTFE emulsion with the gel of PVA/H_3BO_3 as the carrier. The method of introducing H_3BO_3 into spinning dope reduced the PVA addition. The "fibril" structure formed between PVA and H_3BO_3 was observed in the nascent hollow fiber. The assumption of the formation of IFMs between PTFE and $CaCO_3$ was also proposed in this study. And the results were all coincide with the assumption of the PWF measurement and the SEM observation.

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