Bacterial Cellulose and Silica Hybrid Reinforcements in Poly-(vinylidene fluoride) Composite Membranes

Zinian Zhao* and Shanshan Yu

Poly-(vinylidene fluoride) (PVDF), which has a low surface energy, is a common material used for ultrafiltration (UF) membranes. Bacterial cellulose (BC) contains a large number of hydroxyl groups, which has a strong water holding capacity. It can improve the hydrophilicity of PVDF. By means of *in-situ* composite preparation, with the introduction of tetraethoxysilane (TEOS) as silicon source from the outside of BC and polymerizing, hybrid reinforcing material comprised of BC and silica (BC/SiO_2) was achieved which were catalyzed by different acids. After that, by means of a phase separation method with PVDF, composite membranes (PVDF/BC/SiO_2) were prepared. Visible spectrophotometry, thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM) were used to investigate the characteristic of BC/SiO_2 hybrids. The structure and properties of composite membranes were also investigated. After catalysis by acid, SiO_2 particles uniformly adhered to the surface of BC fibers, which resulted in small pores being formed preferentially in the interface of PVDF composite membranes, while reducing the finger-like pores. At the same time the retention of the composite membranes were improved. So both the properties and structure were improved due to the presence of certain BC/SiO_2 hybrid reinforcements.

Keywords: Bacterial cellulose; BC/SiO_2 hybrids; PVDF; Composite Membranes; Water flux; Retention

Contact information: College of Material Science and Chemical Engineering, Tianjin University of Science and Technology, 300457, The Thirteenth Street, Teda, Tianjin, PR China;
** Corresponding author: znzhao@tust.edu.cn*

INTRODUCTION

Poly-(vinylidene fluoride) (PVDF) was used in this work as a matrix material in composite membranes. PVDF has a good chemical stability, heat resistance, and weather resistance. It is widely used in membrane distillation, pervaporation, gas separation, microfiltration, and UF membrane separation fields. But PVDF has a low surface energy and it is hydrophobic. As a result, it is difficult for water to get inside the PVDF membrane during the forming process, which tends to cause a delay in phase separation. Applications of PVDF membranes tend to be limited by two major problems: high driving force required for mass transfer through membranes and a tendency to absorb organics and proteins, which causes the fouling, resulting in the rapid decline of flux. Hydrophilic modification can reduce energy consumption and enhance the ability of membrane fouling (Hou *et al.* 2009).

Bacterial cellulose (BC) can be regarded as an emerging biomaterial that is likely to find increased applications. BC is directly synthesized by microbes such as *Acetobacter* under certain conditions. It has some unique properties such as ultra-high purity and fine, high crystallinity, large surface area, good water imbibition, biodegradability, and ability to be regulated during synthesis. Meanwhile, it cannot pollute the environment. Adding BC into a petroleum-based plastic matrix decreases the environmental pollution caused by the raw materials of petroleum products in a synthetic membrane. Therefore, the modified and blended BC with other polymers to produce high-performance composite materials is of high academic value and has broad potential applications. By studying the properties and the modification principles of BC, there is potential to obtain some meaningful results that can expand the scope of application of BC.

The molecular structure of BC contains a large number of hydroxyl groups. It has a high water retention value, which can be defined as the amount of water held by a given amount of solids, expressed as a percentage. The water retention of BC initially has a value of about 1000%, and after freeze-drying it can still reach 600% (Napoli *et al.* 1975; Yamanaka *et al.* 1989; Wada *et al.* 1993; Yu *et al.* 1999). To some extent, BC can improve the hydrophilicity of PVDF membranes. At the same time, changes of nanoparticles such as composition, properties, process conditions, and other parameters have significant influences on the properties of the composite membranes. The properties of nano-composite membranes can be controlled with more degrees of freedom (Peng and Liu 2007).

The general class of nanocomposite inorganic/organic materials is a fast growing area of research (Zollfrank *et al.* 2007). These new materials combine inorganic nanoparticles such as silica and various polymers, including the most abundant natural polymer, cellulose. The structure of silica is porous. When dispersing it in the system of a casting solution, it will form a network structure and connect with each other. But the blending between BC and SiO_2 is only mechanical. They are only mixed and distributed in spatial position. So tetraethoxysilane (TEOS) is a common precursor used in the synthesis of silica based materials. Our work focuses on the preparation of BC/SiO_2 hybrids which combine the advantages of BC and SiO_2. The sol-gel process of TEOS was performed to deposit sillica on the surface of BC in solutions. An *in-situ* synthesis method was used to prepare BC/SiO_2 hybrids, and the effects of BC/SiO_2 hybrids catalyzed by different acids were also studied.

Two aspects were studied. First, the effects of different species of catalysts were evaluated relative to preparation of BC/SiO_2 hybrids, including the reaction rate, morphology, and components. Second, the effects of BC/SiO_2 hybrids relative to the characteristics of PVDF composite membranes were studied, including kinetics, structure, and properties. In order to get the optimal hybrids and to expand the possibilities and the scope of applications such as to improve the hydrophily and porosity, it is important to learn more about the formation mechanism of the composites to enhance the function of permselectivity of composite membranes.

Hybridization with more than one component in the same matrix provides another dimension to the potential versatility of composite material, offering a range of properties that cannot be obtained with a single type of reinforcement. The present work provides a way to enhance the relative properties of composite membranes. It is devoted to increasing the hydrophilicity and porosity of composite membrane by using various analytical techniques and determined the kinetics of membrane formation and composite membrane properties.

The main finding of this work is that during the synthesis of BC/SiO_2 hybrids, the species of different acids affected the reaction rate, the particle size, the number, and the distribution of SiO_2, which further affected the structure and properties of the composite membranes. The membrane kinetics instrument was used for the determination of the rate of membrane formation. The membrane properties instrument was used to measure the water flux. The ultraviolet and visible spectrophotometer was used to measure the retention. SEM was used for observing the structure of composite membranes. This made it possible to explore the best conditions of formation by analyzing the influence of the properties of BC/SiO_2 hybrids reinforcement on PVDF composite membranes.

EXPERIMENTAL

Materials

Poly-(vinylidine fluoride) (PVDF) was a commercially available fiber grade. The bacterial cellulose (BC) was lab-cultured by *Acetobacter xylinum* M12. The silica was a commercially available amorphous SiO_2 identified as a hydrophilic fumed silica with average primary particle size 7 nm. The silica was used as a mixture with minced BC in this work, expressed as SiO_2-blended in this paper. Ovalbumin, with a molecular mass of M = 43000 g/mole, was a commercially available material. N,N-dimethylacetamide (DMAC) (AR), tetraethoxysilane (TEOS, as silica source) (AR), and H_3PO_4 (AR) were purchased from Jiang Tian Chemical Technology Co. Ltd. (Tian Jin, China). Ammonia (AR), CH_3COOH (AR), HNO_3 (AR), HCl (AR), ethanol (CP), and NaOH (CP) were purchased from the North Chemical Reagent Factory (Tian Jin, China). Glycerol (CP) was purchased from Kaitong Chemical Reagent Co. (Tian Jin, China).

Preparation of BC/SiO_2 Hybrid Materials

An *in-situ* synthesis method was used to prepare BC/SiO_2 hybrids to be used for reinforcement. The aim of this approach was to make use of the excellent absorbent properties of BC. BC was immersed in a solution with specified amounts of ethanol, TEOS, NaOH, and ammonia so that TEOS could be soaked into the interior of BC and adhered to the surface of the BC fibers. Subsequently, in-situ reduction was allowed to occur, forming a hybrid of cellulose and silica. In hybrids, SiO_2 microspheres uniformly distributed in BC fibers and surrounded along BC fibers which were based on a relatively good nano network structure of BC hydrogel.

The formation of BC/SiO_2 hybrid was the result of making use of the interaction between the silicon source and the -OH groups of BC. First, the silica source (TEOS) was uniformly dispersed in the BC filaments, and the hydrolysis reaction occurred under acidic conditions.

A certain amount of minced BC (10.4 g) was added into a specified quantity of ethanol (80 mL), followed by addition of TEOS (4.16 g), NaOH (20 mL), and ammonia (1.4 g) at room temperature. The mixture was stirred for 15 min, and then a specified amount of catalyst (0.01 mol/L) was added. The mixture continued to be stirred for 15 min. The reaction was allowed to proceed for 24 h. The resulting product was washed repeatedly with deionized water to obtain BC/SiO_2 composites by freeze drying (Zheng *et al.* 2007; Barud *et al.* 2008; Cai and Kim 2010; Zeng *et al.* 2011).

Visible Spectrophotometer

The suspension of BC/SiO_2 in the reaction was subjected to suction filtration. A drop of ammonium molybdate was added in the filtrate. The mixture was shaken well. An aliquot of 2 mL reaction solution was removed immediately into the colorimetric cuvette of 1 cm cross-section. Deionized water was used as the reference to calibrate the 100% transmittance level. At the 410 nm wavelength, absorbance (A_m) values of solutions were measured under different conditions.

Reaction Rate Analysis and Morphology Analysis

Drawing of the curve for the reaction rate

The method of silicon molybdenum yellow was employed to measure the content of oligomeric silicon for monitoring the speed of the reaction. In order to convert the results to a reaction rate, the Lambert- Beer law was used, based on an assumption that the absorption of light was proportional to the thickness of the absorbing layer and the concentration of solutions. It was assumed that the influence of the thickness for the absorbing layer and the concentration of solutions contributed linearly to the absorptivity of light, making it possible to convert results and determine the reaction rate. A concentration-absorbance standard curve was drawn from the data and displayed on the screen of the Visible Spectrophotometer (Liu *et al.* 2009).

Thermogravimetric analysis (TGA)

A TGA analyzer was used to investigate the thermal stability of the composite of BC/SiO_2 hybrid. TGA analysis was performed in N_2 from room temperature to 600 ^oC at a heating rate of 10 ^oC min^{-1}.

Infrared Spectroscopy (FTIR)

FTIR spectra of BC and BC/SiO_2 hybrid were obtained with a Nicolet 5700 spectrometer. The sample for FTIR analysis was dispersed in KBr and then powdered in a mortar. Both specimens and KBr were carefully dried before disk preparation and were subjected to FTIR analysis immediately afterwards.

Muffle furnace

The freeze-drying of BC/SiO_2 hybrids were put into a muffle furnace set at 500 ^oC for 4 h to remove BC, making it possible to measure the content of SiO_2 of ash after ignition.

Preparation of the sample of scanning electron microscopy (SEM)

After the freeze-drying of BC/SiO_2 hybrids had been completed, a small amount of each specimen was put on the sample stage to spray gold, and then the structure and morphology of BC/SiO_2 hybrids were observed using the JSM-6380LV SEM.

The prepared PVDF/BC composite membrane splines were soaked in a 50% glycerol solution for 48 h. Then the splines were taken out of the solution and were dried in air naturally. The splines were put in liquid nitrogen to impart brittle fracture. A gold-spray coating was applied to the section of splines by vacuum coating equipment. Finally, the fractured specimens were observed by SEM.

Membrane Performance Testing

Determination of water flux

Determination of water flux of the membrane is generally carried out with velocity filter. Water flux is calculated using the following formula,

$$J=V/(A\bullet t) \qquad (1)$$

where J is water flux ($L/(m^2\cdot h)$), V is filtrate volume (L), A is effective area of membrane (m^2), and t is the required time required for passage of the volume V (h).

After being preloaded for 10 min, the pressure was adjusted to 0.15 MPa while the water flux was being tested. A graduated cylinder was used to measure the water volume for a certain period of time.

Determination of retention

The extent of retention was determined as follows: First, the membrane was preloaded at 0.15M Pa for 10 min. Some filtrate was taken, and its absorbance was measured at a certain wavelength by UV spectrophotometer. The permeate liquid was ovalbumin solution, M=43000, and the wavelength was 280 nm. Then the absorbance was converted to concentration. The retention was calculated by the following formula (Wu and Wang 2000),

$$R = (C_F-C_P)/C_F \times 100\% \qquad (2)$$

where R is retention (%), C_F is the concentration of the separated liquid in raw material liquid (mol/L), and C_P is the concentration of the separated substance in penetration liquid(mol/L).

Determination of light transmittance curve

A light transmittance curve could be obtained by the instrument to measure the phase separation process. The transmittance intensity (voltage value) of the membrane of the casting solution changed with time by light irradiation. This curve can reflect the separation of the start and finish times, that is, the gel kinetics curve. By this means, a sedimentation velocity was obtained for different formulations.

RESULTS AND DISCUSSION

The Effect of Catalysts to BC/SiO_2 Hybrids

If a small amount of acid as a catalyst was added to the BC/SiO_2 hybrid system, it can greatly accelerate the rate of reaction of TEOS, and sometimes it even can be instantly completed. An acidic environment is favourable for the hydrolysis of TEOS, the Si atom is attacked by H_3O^+ in the reaction. A condensation reaction followed hydrolysis, so the main reaction can be described as follows:

$$\text{Si—OH}+\text{HO—Si} \rightarrow \text{Si—O—Si}+H_2O \qquad (3)$$

The Effect of Different Species of Catalysts for BC/SiO_2 Hybrids

The effect of different species of catalysts to the reaction rate of BC/SiO_2 hybrids

Equal amounts of different acids were added individually as catalysts in the same sample to measure the relationship between absorbance and the time of samples, and this was converted to the relationship between concentration and time on the basis of a standard curve. The resulting reaction rate curves are shown in Fig. 1.

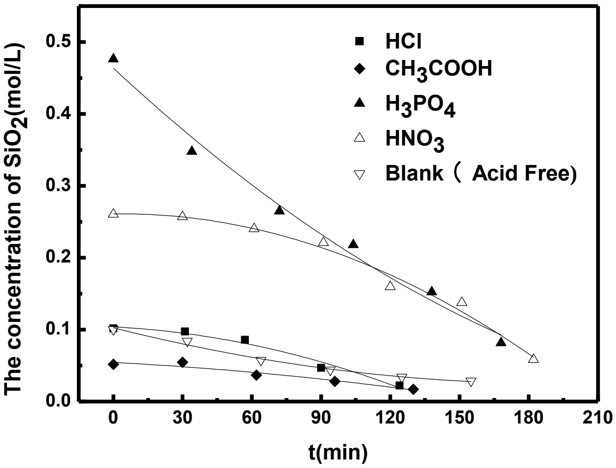


Fig. 1. Effect of different catalysts on the reaction rate of BC/SiO_2 hybrids

As the figure shows, with the addition of an acid catalyst, the reaction rate was varied to different degrees. H_3PO_4 was the fastest, followed by HNO_3. CH_3COOH was the slowest, and it was even slower than the rate of reaction without catalyst (Blank). So this showed that the weak monoacid inhibited the hydrolysis and polymerization of TEOS. The catalytic effect of the strong monoacid HCl was almost the same with the test without catalyst. It could be seen that there was a certain influence of the intensity of the acid catalyst and acid radical ion relative to the reaction rate.

TGA for BC and BC/SiO_2 (HCl) hybrid

In Figure 2, curve “b” represents a thermogravimetric curve for a BC/SiO_2 hybrid catalyzed by HCl, whereas curve “a” corresponds to BC. Based on curve b it is possible to calculate the composition of SiO_2-coated BC fibers. The weight loss ratio was 14.17%. Combining with the thermo-gravimetric ratio of BC, the SiO_2-coated ratio was 73.31%. In the first stage, the weight loss of BC/SiO_2 hybrid was mainly due to the contribution of bound water, the breakage of hydrogen bonds, and the unreacted silicane bonds continuing to undergo dehydration condensation. The second stage of thermal weight loss was caused by the degradation of BC.

The SiO_2-coated ratio was more than 50%, which indicated that the reaction was complete. At the falling section of temperature, with the respect to curve “a”, the slope of curve “b” was reduced. This illustrated that the thermal stability of BC/SiO_2 hybrid was improved. SiO_2 grew along the BC fibers, which completely covered the surface of the BC fibers.

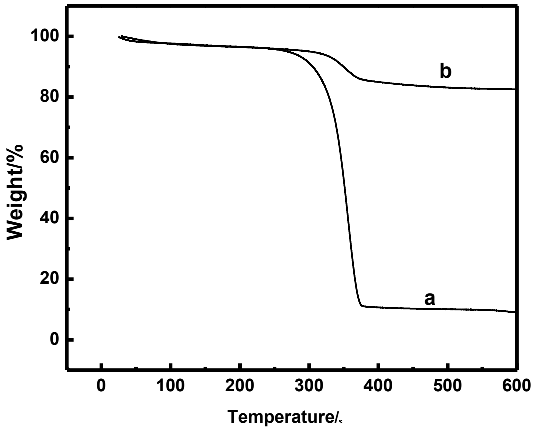


Fig. 2. Curves of TGA, where curve “a” corresponds to BC, curve “b” corresponds to the BC/SiO_2 (HCl) hybrid

FTIR analysis for BC and BC/SiO_2 (HCl) hybrid

The infrared (IR) spectrum of the BC/SiO_2 hybrid catalyzed by HCl is presented in Fig. 3, along with the comparison spectrum of BC. Curve “b” shows two characteristic peaks at 467 cm^{-1} and 804 cm^{-1}. The absorbance at 467cm^{-1} was assigned as the bending vibration absorption peak of Si-O-Si bond, whereas 804 cm^{-1} was assigned as the symmetric stretching vibration peak of Si-O-Si bond. The IR spectrum demonstrated that the hybrid had incorporated SiO_2 successfully. It was not simply blended.

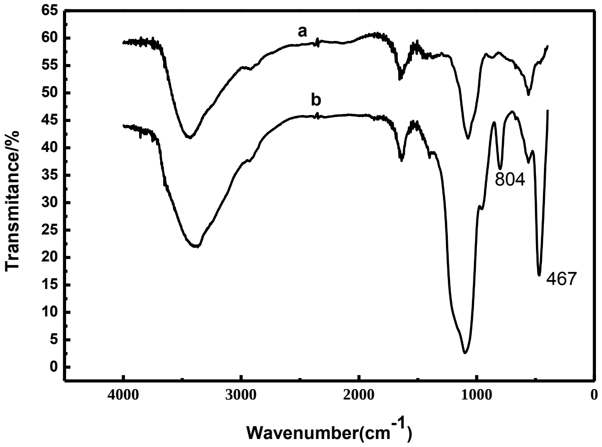


Fig. 3. IR Spectrogram, where curve “a” corresponds to BC and “b” is BC/SiO_2 (HCl) hybrid

Effect of the species of catalyst to the components of BC/SiO_2 hybrids

Figure 4 shows the SiO_2 contents of different BC/SiO_2 hybrids for high temperature calcination by muffle furnace. After calcination, the BC fibers disappeared, and SiO_2 particles remained. The figure shows that the amount of generated SiO_2 catalyzed by HCl was the largest, followed by CH_3COOH. The HNO_3 catalysis resulted in the least amount of SiO_2, which was even less than the blank sample. In general, the smooth and steady reaction rate provided time to disperse the SiO_2 particles uniformly on the BC fibers.

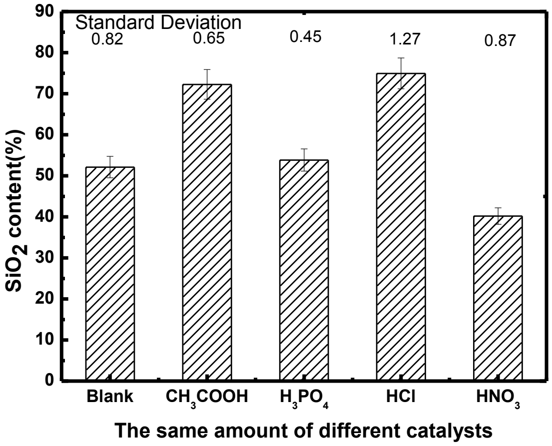
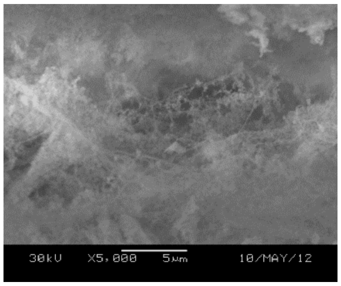


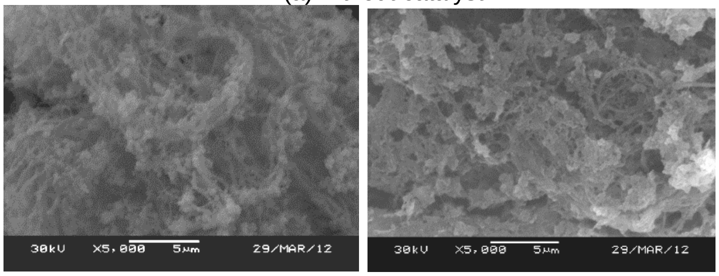
Fig. 4. Composition distribution of BC/SiO_2 hybrids by using different catalysts

Effect of different species of catalysts to the morphology of BC/SiO₂ hybrids

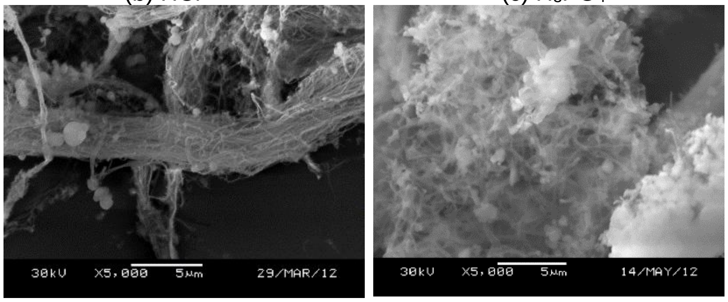
Figure 5 shows the structure and morphology of BC/SiO_2 hybrids that were catalyzed by different acids.



(a) without catalyst



(b) HCl (c) H_3PO_4



(d) CH_3COOH (e) HNO_3

Fig. 5. Effect of different catalysts on the SEM photographs of BC/SiO_2 hybrids

From the figure it can be seen that the BC of the blank sample without catalyst was uniformly tiny, and there were many tiny SiO_2 particles attached to the BC. This was because the reaction rate was slow without the catalysis of acids. The condensation reaction was smooth and steady after the hydrolysis of TEOS so that the generated SiO_2 particles were uniformly distributed on the surface of BC.

Compared to tests carried out in the absence of acid-catalysts, the morphology of hybrids prepared with HCl changed a little, with just a slight increase in the amount of SiO_2 particles, which showed that HCl played a role of a catalyst. After HNO_3 or H_3PO_4 was added, the composite fibers were thickened, and the generated SiO_2 particles size were enlarged. The SiO_2 particles partly agglomerated because the reaction rate of the two acids were so fast that SiO_2 particles had no time to disperse uniformly. Since the reaction rate of CH_3COOH was slowest, after catalyzed by CH_3COOH, the reaction rate of SiO_2 was slow and the particles were tiny and attached on the surface of BC.

Effect of BC/SiO_2 Hybrids to PVDF/BC/SiO_2 Composite Membranes

The BC/SiO_2 hybrids of different catalysts

HCl, H_3PO_4, CH_3COOH, and HNO_3 were employed as the reaction catalysts for repeated filtration, washing, and lyophilization to obtain BC/SiO_2 hybrids, which were added into the PVDF respectively to obtain the PVDF/BC/SiO_2 composite membranes. These will be referred to as the I, II, III, and IV composites in the following discussion.

Effect of BC/SiO_2 hybrids to the kinetics of composite membranes

Table 1 gives the rate of membrane formation after adding different BC/SiO_2 hybrids. The composite V was prepared without any acid catalyst, leading to the lack of the constraint of valence bond force between the blended BC and SiO_2, so they were weakly combined. At the same time the amount of SiO_2 blended was so large that there were wider aisles for non-solvent to exchange. The solvent was more likely to be replaced, so the transfer rate and the rate of membrane formation was the fastest. After the BC/SiO_2 hybrid was added, the membrane formation rate of III composite membrane was the fastest, I was the second, and II and IV were the slowest.

Table 1. Effect of BC/SiO_2 Hybrids on Membrane Formation Kinetics of PVDF/BC/SiO_2 Composite Membranes

Composite membrane	Ⅰ	Ⅱ	Ⅲ	Ⅳ	BC/SiO_2 blended（Ⅴ）
Slope	3.1291	2.2401	3.7308	2.5492	4.1344
Standard deviations	0.72	0.91	0.34	2.19	0.3

Remark: The content of BC and BC/SiO_2 hybrid was 0.4%.The commercially available silica was mixed into the composite membrane directly and was named SiO_2 blended. In the following text, the PVDF/BC/SiO_2 blended composite membrane is referred to as composite Ⅴ.

The rates of BC/SiO_2 hybrids catalyzed by HCl and CH_3COOH were slow. The size of SiO_2 particles became smaller; their superficial area was large and they uniformly covered the surface of BC fibers. The formative BC/SiO_2 hybrid was the most homogeneous, so it was judged to be the most suitable to improve the cellular structure of the formative membrane which undergoes a phase separation. It caused the PVDF and BC fibers to be dispersed more uniformly, and the sedimentation rate of BC fibers was homogenized after added in PVDF. The transfer rate of coagulation bath was increased, which improved the connectivity of hybrids and increased the contact surface between solvent and non-solvent. The rate of membrane formation was also improved.

Because the reaction rate of composites catalyzed by H_3PO_4 and CH_3COOH was fast, the generated SiO_2 particles had no time to cover on the surface of BC fibers. On the contrary SiO_2 particles gathered into big ones, and the interaction between BC and SiO_2 particles was weak.

The dispersion deteriorated, and the contact surface with the non-solvent was small when the BC/SiO_2 hybrids were added into the coagulation bath, which influenced the transfer rate of coagulation bath and reduced the rate of membrane formation.

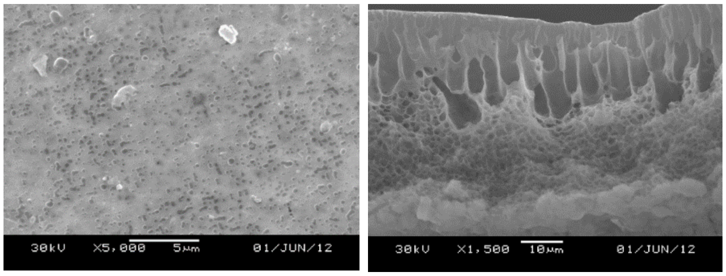
Effect of BC/SiO_2 hybrids to the structure of composite membranes

Figure 6 shows SEM photographs of the surface and fracture of the cross-section of PVDF/BC/SiO_2 and PVDF/BC/SiO_2 blended composite membranes. The adjunction of BC/SiO_2 hybrid made the surface of the composite membrane become denser and reduced finger-like holes in the fracture surface. On the one hand, this was due to the strong surface polarity of SiO_2 that the SiO_2 particles coated tightly around the BC fibers, which interacted with the polar hydroxyl of the surface of BC fibers to form hydrogen bonds. It reduced the polarity of the surface of BC fibers. On the other hand, the generated SiO_2 was smaller than the blended SiO_2. To a certain degree, this improved the dispersion of BC/SiO_2 hybrids in the coagulation bath, which made the dispersion between BC and PVDF more uniform, so that the sedimentation velocity of BC and PVDF was homogenized.

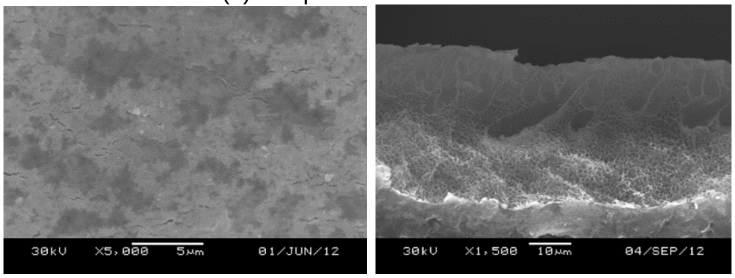
The fast gel process helped the conformation of finger-like holes, so that the membrane formation rates of II, III, and IV composite membranes were reduced. Therefore, the cross section structure showed that the finger-like holes had been decreased. The reaction rates of BC/SiO_2 hybrids catalyzed by HCl and CH_3COOH were smooth. Large numbers of generated SiO_2 particles covered the surface of BC fibers uniformly. At this time, the hybrid could be dispersed well in the PVDF, and the membrane formation rate was increased.

The holes of the cross section structure were increased, and at the same time the cortex was thickened, as shown in Figs. 6 (a) and (c). Furthermore, the rate of phase separation of composite membrane was fast, so that the concentration of polymer in the initial phase interface was low, which was helpful to the growth of the polymer-poor nucleus and the development of large pore structure. As a result, the finger-like holes were enlarged, but they were fewer in quantity.

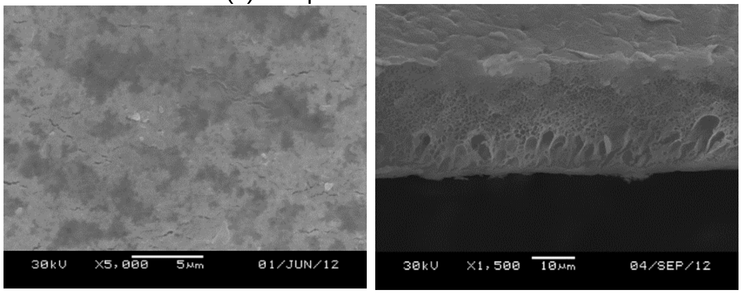
The reaction rates of BC/SiO_2 hybrids catalyzed by H_3PO_4 and CH_3COOH were fast, and the generated SiO_2 particles mostly remained granular, but little connected with the BC fibers. There was limited improvement in the dispersion of the system for putting the BC/SiO_2 hybrids into the coagulation bath of the composite membrane. The transfer rate of solvent declined, the membrane formation rate and the phase separation of the composite membrane declined slightly, which was not conductive to the polymer-poor nucleus, and it limited the development of large holes. There were a few finger-like holes in the cross structure of membrane, as shown in Fig. 6 (b) and (d).



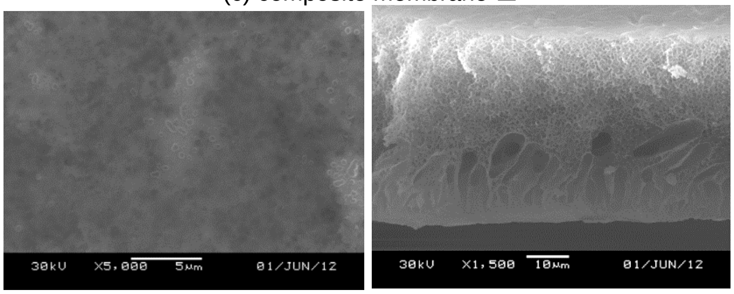
(a) composite membrane Ⅰ



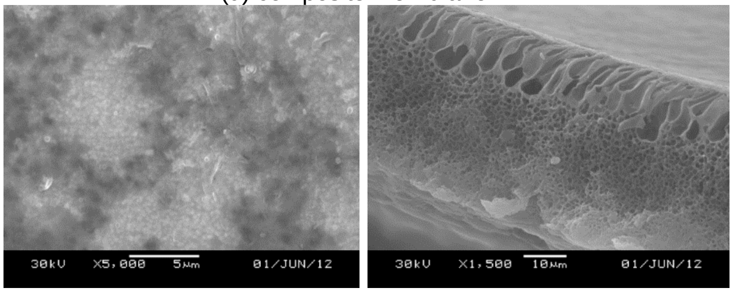
(b) composite membrane Ⅱ



(c) composite membrane Ⅲ



(d) composite membrane Ⅳ



(e) composite membrane Ⅴ

Fig. 6. Effect of BC/SiO_2 hybrids on structure of PVDF/BC/SiO_2 composite membranes

Effect of BC/SiO_2 hybrids to the properties of composite membranes

Figure 7 shows the influence of BC/SiO_2 hybrids on the properties of PVDF/BC/SiO_2 composite membranes. The last group corresponds to the properties of the composite membrane achieved by adding blended BC/SiO_2. As shown, compared with blended BC/SiO_2, the retention of BC/SiO_2 hybrid was improved greatly, but the water flux declined slightly. The retention of II composite membrane was the highest. So the retention was proportional to the reaction rate of BC/SiO_2 hybrid catalyzed by acids and inversely proportional to the amount of SiO_2 particles. The retention of V composite membrane was the lowest.

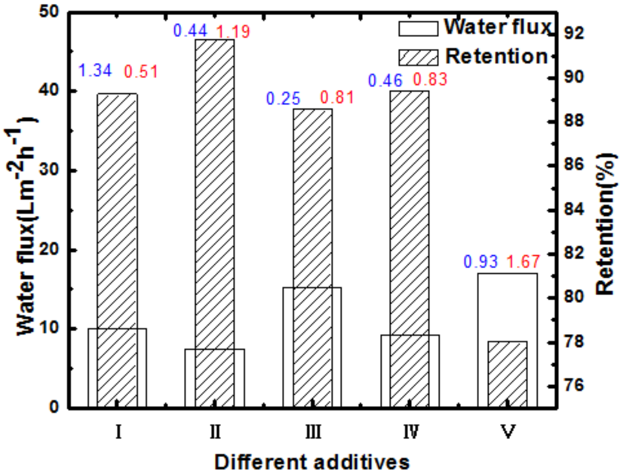


Fig. 7. Effect of BC/SiO_2 hybrids on properties of PVDF/BC/SiO_2 composite membranes
Remark: The blue number is the Standard Deviation of Water flux and the red one is the Standard Deviation of Retention.

The V composite membrane, without the use of an acid catalyst, led to the lack of the constraint of valence bond force between BC fibers and blended SiO_2, which were weakly combined. At the same time, the amount of blended SiO_2 was so large that there were wider aisles for non-solvent to exchange. The solvent was more likely to be replaced, so that the transfer rate and the rate of membrane formation were the fastest. Also the retention was the lowest and the water flux was the highest. The addition of BC/SiO_2 hybrid improved the dispersion of the BC/SiO_2 in the composite membranes, and at the same time, the sedimentation rate of BC and PVDF was homogenized, which made the membrane formation rate decline and reduced the number of finger-like holes. These changes led to a decline of water flux in the composite membranes. In the BC/SiO_2 hybrids catalyzed by HCl and CH_3COOH, SiO_2 particles were tiny. They had a large surface area and they covered BC fibers densely and uniformly. After the BC/SiO_2 hybrids were added into the PVDF membrane, the retention of PVDF/BC/SiO_2 was improved greatly relative to the PVDF/BC SiO_2 (blended), and a better interface of micropores was formed. The refinement effect was obvious. Compared to the composite membrane catalyzed by H_3PO_4 and HNO_3, the contact surface of the non-solvent was large, and the connectivity of the membrane micropores was improved. So the water flux was larger than the latter two.

Thus, the performance of membrane III was optimal. On the one hand, the water flux decreased slightly relative to the blended PVDF/BC SiO_2, but it was larger than the others. On the other hand, the retention was improved greatly. So the composition met the requirement of the preparation of the optimum performance for the composite membrane, the goal of which was to achieve a certain retention with a large water flux.

CONCLUSIONS

1. As the acid catalyst, HCl resulted in the largest amount of generated SiO_2 particles comprising the BC/SiO_2 hybrids, and the reaction rate was same as the control with no catalyst. The reaction rate of the hybrid catalyzed by CH_3COOH was reduced, which led to slightly less the amount of SiO_2 particles than the former, but the structure of the cellulose was clear and the SiO_2 particles were tiny and distributed uniformly.
2. PVDF/BC/SiO_2 composite membranes were prepared by adding BC/SiO_2 hybrids catalyzed by different acids, which reduced the amount of finger-like holes, forming a better porous interface, and it improved the retention performance of the composite membrane. The generated SiO_2 particles of BC/SiO_2 hybrid catalyzed by CH_3COOH were tiny and had a large surface area, covering the surface of BC fibers uniformly. After they were put into the PVDF, the effect of refining the pores was obvious, and the micropores with a large contact area were tiny and uniformly distributed, allowing a favorable interaction with non-solvent. This combination of features gave a high retention and a larger water flux.

REFERENCES CITED

Barud, H. S., Assuncao, R. M. N., Martines, M. A. U., Dexpert-Ghys, J., Marques, R. F. C., Messaddeq, Y., and Ribeiro, S. J. L. (2008). “Bacterial cellulose-silica organic-inorganic hybrids,” *Journal of Sol-Gel Science and Technology* 46(3), 363-367. DOI: 10.1007/s10971-007-1669-9

Cai, J., and Kim, J. (2010). “Bacterial cellulose/poly(ethylene glycol) composite： Characterization and first evaluation of biocompatibility,” *Cellulose* 17(1), 83-91. DOI: 10.1007/s10570-009-9362-5

Hou, L., Fan, P., and Lu, Y. (2009). “The modified progress of poly-(vinylidene fluoride) membranes,” *Environmental Research and Monitoring* 22(1), 66-67.

Liu, L., Zhang, N., Liu, Y., Li, Y., Zhuang, Y., and Jin, Z. (2009). “Determination of silicon oxide in silica fume by molybdosilicate yellow spectrophotometry,” *Journal of Metallurgical Analysis* 29(10), 63-65. DOI: 10.3969/j.issn.1000-7571.2009.10.015

Napoli, C., Dazzo, F., and Hubbel, D. (1975). “Production of cellulose microfibrils by rhizobium,” *Applied and Environmental Microbiology* 30(1), 123-131.

Peng, L., and Liu, S. (2007). “The influence of nano-silica to PVDF ultrafiltration membrane for the gel process and structure,” *Membrane Science and Technology* 27(4), 42-44.

Wada, M., Sugiyama, J., and Okano, T. (1993). “Native cellulose on the basis of two crystalline phase (I_α/I_β) system,” *Journal of Applied Polymer Science* 49(8), 1491-1496. DOI: 10.1002/app.1993.070490817

Yamanaka, S., Watanabe, K., Kitamura, N., Lguchi, M., Mitsuhashi, S., Nishi, Y., and Uryu, M. (1989). “The structure and mechanical properties of sheets prepared from bacterial cellulose," *Journal of Materials Science* 24(9), 3141-3145. DOI: 10.1007/BF01139032

Yu, B., Quan, H., and Bian, Q. (1999). "Novel biopolymer-microbial cellulose and its commercial applications," *Journal of Cellulose Science and Technology* 7(3), 42-46.

Zeng, W., Wang, Y., and Dong, L. (2011). "The preparation of silica nanotube basing on the bacterial cellulose template," *Journal of Tianjin University of Science and Technology* 26(1), 31-35. DOI: 10.3969/j.issn.1672-6510.2011.01.008

Zheng, B., Li, Q., and Zhu, P. (2007). "Preparation and characterization of silica nanotube by template method," *Journal of Chemical Industry and Engineering (China)* 58(10), 2641-2646.

Zollfrank, C., Scheel, H., and Greil, P. (2007). "Regioselectively ordered silica nanotubes by molecular templating," *Adv. Mater*. 19(7), 984-987. DOI: 10.1002/adma.200601548

Wu, K., and Wang, B. (2000). "The measurement of the interception performance of ultrafiltration membrane," *Tianjin Chemical Industry* 14(2), 24-26.

Article submitted: July 25, 2014; Peer review completed: September 2, 2014; Revised version received and accepted: September 23, 2014; Published: October 2, 2014.