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Preparation and characterizations of a new PS/TiO_2 hybrid membranes by sol–gel process

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Abstract

New organic–inorganic hybrids based on PS/TiO_2 hybrid membranes were prepared by sol–gel and phase inversion process. The membranes were characterized in terms of morphology, structure, hydrophlicity, UF performance and thermal stability. The results showed that macrovoids were nearly suppressed with formation of a sponge like membrane structure. The TiO_2 particles were uniformly dispersed in membrane. The nanodispersed inorganic network formed after sol–gel process and the strong interaction between inorganic network and polymeric chains led to the improvement of porosity and thermal stability. In particular hydrophilicity and permeability increased drastically with the increasing of TiO_2 content in the range of 0–9.3 wt%, without changing retention properties of membrane. However, high-TiO_2 concentration induces nanoparticles aggregate, resulting in the decline of hydrophilicity and permeability. Thus, PS/TiO_2 hybrid membranes with proper TiO_2 content are desirable to meet some specific requirements in industrial separation.

Keywords: Polysulphone; Titanium dioxide; Sol–gel process

1. Introduction

Currently, polymers are still the main membrane materials in membrane technology with the advantages of good flexibility, toughness, and separation properties. However, a limited chemical, mechanical and thermal resistance restricts their applied scale. As reported in literatures [1,2], ceramics membranes have higher thermal and chemical resistance and longer lifetime, but they are expensive with poor flexibility and low-separation performance. Hybrid materials can combine basic properties of organic and inorganic materials and offer specific advantages for the preparation of artificial membranes with excellent separation performances, good thermal and chemical resistance and adaptability to the harsh environments, as well as film forming ability [3–6]. Thus, organic–inorganic hybrid materials as new membrane materials have attracted more and more attentions. The sol–gel technique is one of the most extensively applied method for preparation of organic–inorganic nanomaterials, which allows the formation of inorganic frameworks under mild condition and incorporation of minerals into polymers, resulting in an increased chemical, mechanical and thermal stability without obviously decreasing the properties of the polymers [7–9]. Furthermore, the remained hydrogen bond clusters at the surfaces of the materials after the sol–gel reaction improves the membrane hydrophilicty and enhances hybrid material stability [10–16].

Polysulfone (PS) is one of the most extensively applied ultrafiltration (UF) membrane materials in industry area for mechanical strength, compaction-resistance, chemical stability, thermal resistance and in wide pH value range application (2–12). But its hydrophobic nature is also well-known, which results in the adsorption and deposition of hydrophobic solute on the membrane surface [17]. The adsorption and deposition can cause severe membrane fouling due to the formation of thick gel-layer and the block of the pores, which will result in the flux decline and short-life of membrane. Although the modification of PS have been widely explored such as the modification of membrane surface [18] and membrane material [19], the problems such as tradeoff between permeability and selectivity, the process complexity, the manufacturing costs and stability still remain to be unsolved. Titanium dioxide (TiO_2) has been the focus of numerous investigations for innocuity, resisting and

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decomposing bacterias, UV-proof and super hydrophilicity [20] in recent years. Therefore, it has been applied to a variety of problems of environmental interest in addition to water and air purification [21].

The aim of this work was to prepare a novel PS/TiO_2 organic–inorganic hybrid UF membrane with high hydrophilicity and permeability, mechanical and thermal stability by sol–gel and phase inversion process. The preparation of PS/TiO_2 hybrid membranes with finely dispersed TiO_2 in the polymer matrix was discussed. The effects of existence of TiO_2 nanoparticles and resulting in organic framework on membranes properties were investigated by examining UF performances, hydrophilicity, thermal analysis of membranes, as well as the microstructures of membrane.

2. Experimental

2.1. Materials

PS (S180) was purchased from Shanghai Shupeng, China. Polyvinylpyrrolidone (PVP, K30) was obtained from BASF, Germany. *N*,*N*′-Dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidinone (NMP), tetrabutyltitanate (Ti $(OBu)_4$), were obtained from Shanghai Chemical Reagent Company (China) and used without further purification. Acetate acid and hydrochloric acid (HCl, 36–38%) were of analytical grade (from Beijing Chemical Reagent Company, China) and used as received. The Bovine serum albumin (BSA, 67 kDa) was purchased from Beijing Dingguo Biologic Tech (China).

2.2. TiO_2 sol preparation

1.0 mL acetate acid and 10.0 mL $Ti(OBu)_4$ were added to 10.0 mL NMP with stirring (solution A). 0.3 mL HCl in 2.0 mL deionized water was added to another 10.0 mL NMP (solution B). Then solution B was added dropwise to solution A with vigorous stirring for 2 h at room temperature. After mixing uniformly, stable, transparent and flaxen TiO_2 sol was obtained with pH 4.0 adjusted by HCl.

2.3. Membrane preparation

TiO_2 sol with different content (0, 1.3, 3.3, 5.3, 7.3, 9.3, 11.9, 14.6, and 17.2 wt%) was added dropwise to the casting solution of DMAc and NMP (vol_{DMAC}:vol_{NMP} = 4:1) containing 18 wt% PS and 4 wt% additive PVP with constant stirring for 24 h. The above mixture solution was evacuated for 24 h to remove air bubbles and then was poured onto a glass plate with a doctor blade (thickness: 200 μm) at room temperature. After exposed in air for 10 s, the casting solution on glass was immediately immersed in the ethanol/water (20:80 in volume) bath. The resulting membrane was transferred to a room-temperature water bath and stand for 1–2 days to remove off the remaining solvent and make Ti $(OBu)_4$ hydrolyzed fully. The membrane was stored in demineralized water containing 1% formaldehyde to avoid bacteria growth.

2.4. Membrane characterizations

2.4.1. Morphology observation

Membrane surfaces and cross sections are observed by means of JSM-5500 LV scanning electron microscope (SEM, Japan electron). All specimens were freeze–dried and coated with a thin layer of gold before observation. Cross-section was prepared by fracturing the membranes in liquid nitrogen.

2.4.2. Porosity calculation and the X-ray diffraction (XRD) analysis

Porosity (Pr, %) was calculated as a function of the membrane weight.

$$\mathrm{Pr} = \frac{W_w - W_d}{Sddm} \times 100\%$$

W_w and W_d, weights of membrane at equilibrium swelling with water and at dry state, respectively, S the area of the membrane, d the average thickness of the membrane, dm the density of water.

The membrane XRD patterns were recorded on a D/max-rB diffractometer (Japan) equipped with graphite monochromated Cu Kα radiation (λ = 0.15405 nm) operated at 50 mA and 50 kV from 10 to 80°.

2.4.3. UF performances and hydrophilicity

The water permeability of the membranes was measured with an SCM 300 ultrafiltration cup (ecologic center, Shanghai) fed with demineralized water for 15 min. The test was repeated until the water permeability remaining constant. The retention was described as molecular weight of BSA. The tests were also carried out with an SCM 300 ultrafiltration cup fed with an aqueous solution of BSA (100 mg/mL) for 15 min. Operating conditions were: room temperature, transmembrane pressure of 1 bar and a tangential water velocity of 3 m/s. The contact angle between water and the membrane surface was measured to evaluate the membrane hydrophilicity, using a DSA 10-MK2 contact angle goniometer (KRÜSS, Germany). To minimized experimental error, the contact angles were measured 8 times for each sample and then were averaged.

2.4.4. Thermal analysis

The thermal stability of hybrid membranes was evaluated by thermogravimetric analysis (TGA, Perkin–Elmer Pyris Diamond). The TGA measurements were carried out under nitrogen atmosphere at a heating rate of 10 °C from 50 to 800 °C. Differential scanning calorimetry (DSC, Perkin–Elmer DSC7) measurements were performed on the hybrid membranes from 50 to 300 °C at a heating rate of 10 °C. The first scan was run to 300 °C for 10 min to destroy any initial thermal history, and then the samples was cooled to 50 °C to start the second scan.

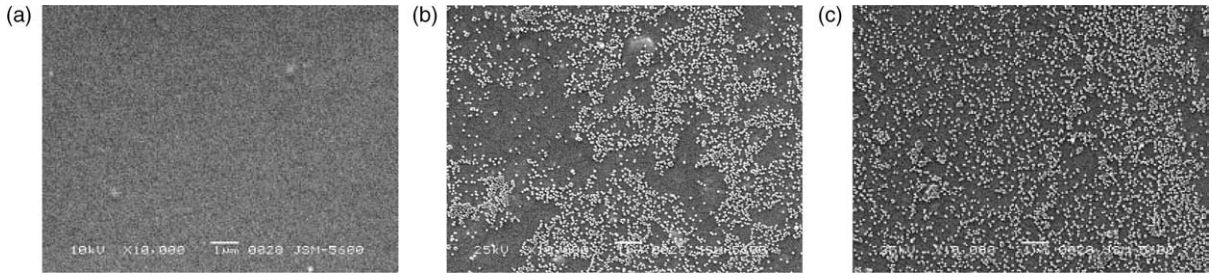

Fig. 1. SEM pictures of PS/TiO_2 composite membranes with different TiO_2 concentration: (a) 0 wt%, (b) 5.3 wt%, (c) 7.3%.

3. Results and discussion

3.1. Membrane morphology

The morphologies of PS and PS/TiO_2 membranes were observed by SEM. Fig. 1 shows that there are an amount of TiO_2 nanoparticles packed by polymers or aggregates of TiO_2 nanoparticles adsorbing or embedding on the surface of PS/TiO_2 hybrid membrane (Fig. 1(b) and (c)) compared with PS membrane (Fig. 1(a)). This phenomena indicates that the drastic increase in casting solution viscosity caused by addition of TiO_2 sol and the interaction caused by adsorption between TiO_2 and polymers lead to nanoparticles move difficultly and adsorbed or embed in the skinlayer.

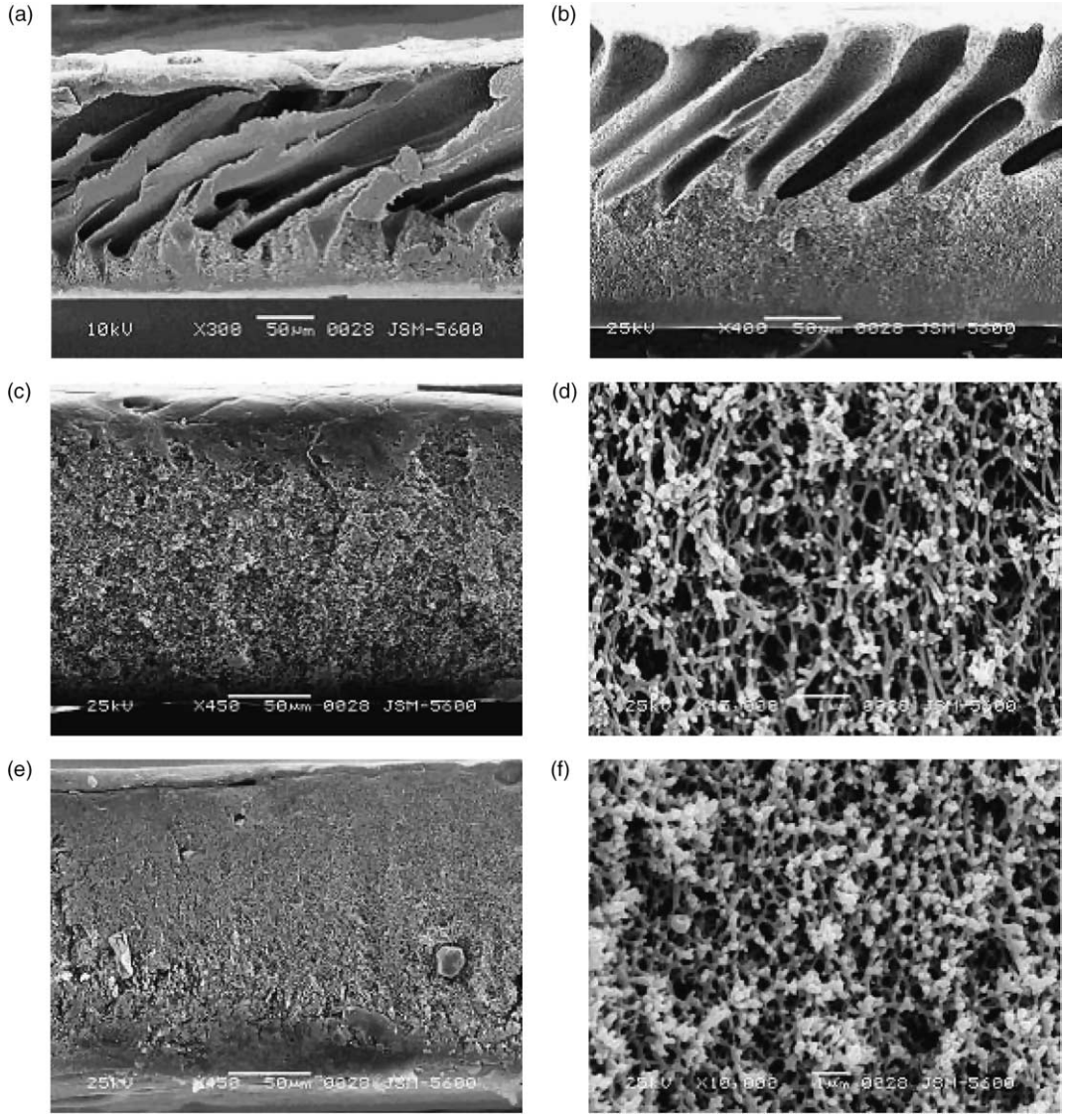

Fig. 2. SEM micrographs of cross-section of PS/TiO_2 membranes with different TiO_2 concentration: (a) 0 wt%, (b) 3.3 wt%, (c) 9.3 wt%, (d) c's local magnifying figure, (e) 14.6 wt%, (f) e's local magnifying figure.

Table 1
Porosity of PS/TiO_2 hybrid membrane with different TiO_2 content

TiO_2 concentration (wt%)	Porosity (%)
0	42.9
3.3	77.5
9.3	84.7
14.6	86.3

Fig. 2 shows that with the increase in the TiO_2 concentration, the topical asymmetric structure of membrane (Fig. 2(a)) becomes faint, the thickness of skinlayer increases (Fig. 2(b)) and the structure of sublayer undergoes a transition from finger like to sponge like structure (Fig. 2(c)). The increase in the viscosity of the casting solution due to the addition of TiO_2 sol slows down the exchange rate of solvent (DMAc/NMP)/nonsolvent (ethanol/water) and results in a delayed demixing process, with macrovoids suppression [22]. According to the hypothesis of McKelvey and Koros [22], macrovoids are initiated by nucleation of the polymer-lean phase just beneath the skinlayer, and its growth lies on the rate difference between the indiffusion rate of nonsolvent to casting solution and the diffusion rate of the solvent to coagulation bath. This rate difference induces a nonsolvent concentration gradient in casting solution, which forms a drive force to cause the macrovoids growth. With the increase in casting solution viscosity induced by addition of TiO_2 sol, the diffusion of nonsolvent slows down greatly and nonsolvent concentration decreases. Consequently, the formation or the growth of macrovoids in membranes is suppressed, and a sponge like structure with entrapped TiO_2 particles is formed (Fig. 2(d)) [23–27]. So, PS/TiO_2 hybrid membranes present a morphology with decreased or eliminated macrovoids, and as consequences, an increase in resistance and mechanical strength.

3.2. Porosity and XRD analyses

The porosity of the membrane is shown in Table 1 and in the magnification of sublayer membrane (Fig. 3), respectively. Shrinkage of organic phase during the precipitation process of wet-casting polymeric membranes builds up stress between polymer and TiO_2, with consequent formation of pores. Fig. 4 shows the XRD diffraction patterns of TiO_2 nanoparticles, PS membrane and PS/TiO_2 hybrid membrane. The pattern of TiO_2 crystal powder has three crystalline characteristic peaks at 2θ 25.32, 37.86 and 48.06°, which agree with the literature report [28], and the pattern of hybrid membrane has also three crystalline characteristic peaks at 2θ of 28.06 , 38.76, and 48.1° that is analogous with the characteristic peaks of TiO_2 crystal powder in addition to the dispersion peak of amorphous PS. This indicates that tetrabutyltitanate has formed TiO_2 crystal through hydrolytic reaction during the preparation of PS/TiO_2 hybrid membrane.

3.3. Membrane hydrophilicity and UF performances

3.3.1. The hydrophilicity of membranes

The contact angle data of PS/TiO_2 hybrid membranes with different TiO_2 concentration listed in Table 2 shows that the membrane hydrophilicity is improved by addition of TiO_2 sol. This fact is due to the presence of TiO_2 nanoparticles generated by tetrabutyltitanate hydrolysis containing an amount of hydroyl groups, responsible of the hydrophilicty increase. However, the contact angle increases when TiO_2 concentration is over 11.9 wt% due to nanoparticles aggregate, resulting in decreasing of hydroxyl groups number. After 15 days of immersion in water bath, the hydrophilicity is highly maintained with the same trend, due to the strong interactions between TiO_2 and polymers.

3.3.2. UF performance of membranes

The influence of TiO_2 concentration on permeability and retention is investigated through UF experiments. Fig. 5 shows that the membrane permeability increases with the concentration of TiO_2, with a peak value at 9.3 wt%. However, higher TiO_2 concentration leads to the decrease in permeability. An increase in porosity and hydrophilicity of membrane enhances greatly the permeability greatly. However, high-TiO_2 sol concentration produces highly viscous casting solution which slows down the formation process of hybrid membrane and causes to form a thicker skinlayer and a compact network sublayer containing considerable TiO_2 particles blocking membrane pores and thereby producing a negative effect on permeability. It should be noted that retention of hybrid membrane about BSA kept almost unchanged compared to the PS membrane (Fig. 5) owing to the balance between porosity increase and compact structure of organic–inorganic network.

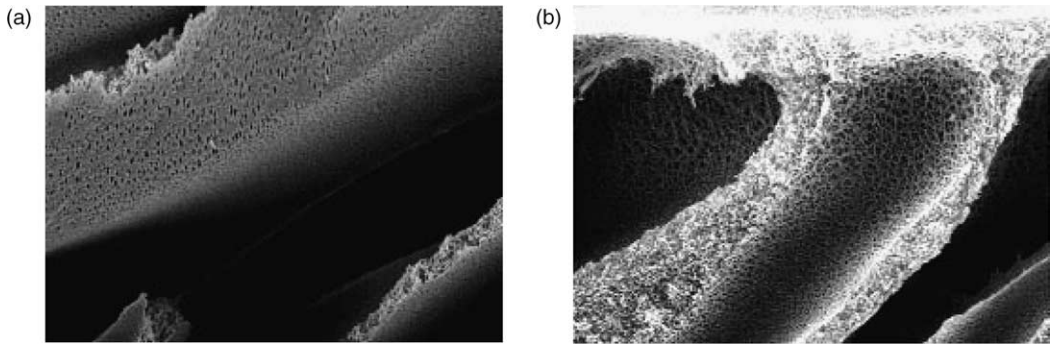

Fig. 3. The SEM images of the pore density of PS membrane (a) and PS/TiO_2 hybrid membrane with 3.3 wt% TiO_2 (b).

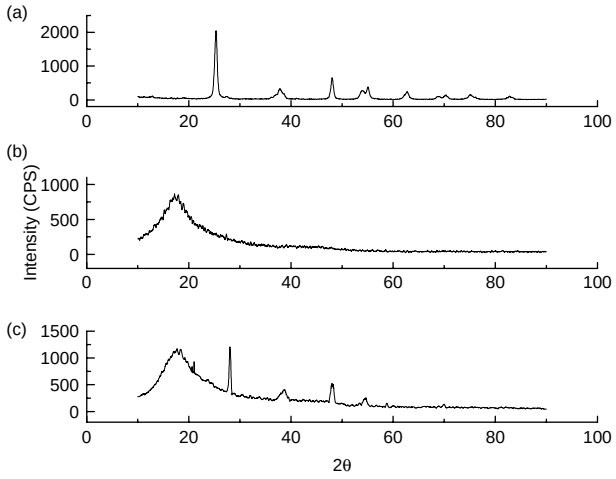

Fig. 4. X-ray diffraction patterns of TiO_2 powder (a) PS membrane (b) and PS/TiO_2 hybrid membrane (c).

Table 2
Contact angle of PS/TiO_2 hybrid membranes with different TiO_2 content

Sample number	TiO_2 concentration (wt%)	Contact angle (°)
1	0	87.7
2	1.3	76.2
3	3.3	64.7
4	5.3	50.6
5	7.3	41.3
6	9.3	32.2
7	11.9	38.4
8	14.6	43.1
9	17.2	49.7

Thus, PS/TiO_2 hybrid membranes possess superior permeability and unchanged retention.

3.4. Thermal properties

The thermal analysis results of PS/TiO_2 hybrid membrane are illustrated in Figs. 6 and 7, respectively. It can be seen that the discomposing temperature (T_d, defined as the temperature at 3% weight loss) and T_g of hybrid membrane increase with the increasing of TiO_2 content reaching at 17.2 wt% the highest values: T_d and T_g are enhanced of 54.2 and 13.21 °C, respectively, compared with polymeric membrane. We can reasonably conclude that interaction of hydrogen bond or other coordinate bonds between TiO_2 inorganic network formed after sol–gel process and polymeric chains, restrict the thermal action of macromolecules, increasing the rigidity of macromolecular chain and enhancing the energy needed by polymeric chain movement and breakage.

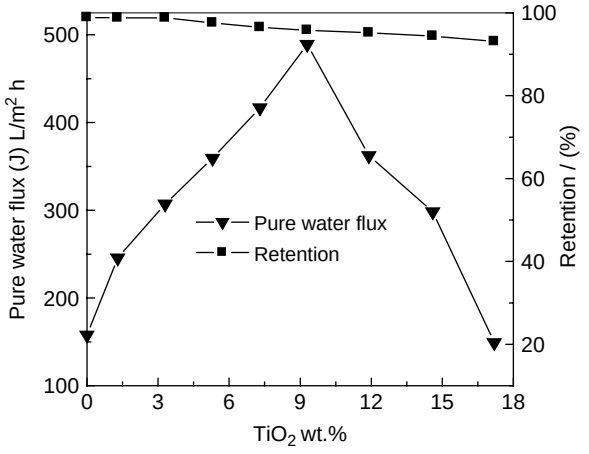

Fig. 5. Pure water flux and retention of PS/TiO_2 hybrid membranes as a function of TiO_2 concentration.

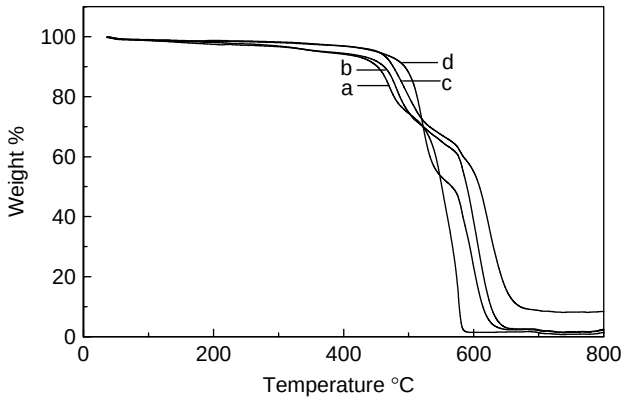

Fig. 6. TG curves of PS/TiO_2 hybrid membranes with different TiO_2 content:(a) 0 wt%, T_d 471.95 °C; (b) 5.3 wt%, T_d 481.22 °C; (c) 9.3 wt%, T_d 496.02 °C; (d) 17.2 wt%, T_d 522.37 °C.

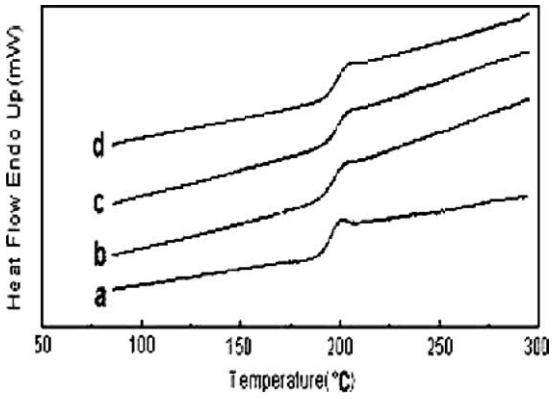

Fig. 7. DSC thermograms of PS/TiO_2 composite membrane versus TiO_2 concentration:(a) 0 wt%, T_g 185.02; (b) 5.3 wt%, T_g 188.36 °C; (c) 9.3 wt%, T_g 191.48 °C; (d) 17.2 wt%, T_g 198.23 °C.

4. Conclusions

New organic–inorganic PS/TiO_2 hybrid membranes were prepared by sol–gel and phase inversion process. The microstructure, porosity, hydrophilicity, UF performance and thermal stability of hybrid membrane are improved apparently by an appropriate choice of TiO_2 concentration. The main conclusions from the results of this study were listed as follows:

1. Macrovoids are restricted and eliminated, the topical asymmetric structure of membrane becomes faint and undergoes a transition from macrovoids to network pores,

consequently the compact resistance of membrane is enhanced.

2. A net structure with inorganic network impenetrating with polymeric networks each other and TiO_2 particles as cross-linking spots after sol–gel process is formed due to the interaction of hydrogen bond or other coordinate bond between TiO_2 inorganic network and polymeric chains, as morphology and excellent thermal properties of hybrid membranes prove.
3. The hybrid membranes exhibit extraordinary hydrophilicity, increased porosity and superior permeability with unchanged retention properties in contrast with polymeric membranes.

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