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Preparation of poly(vinylidene fluoride)(pvdf) ultrafiltration membrane modified by nano-sized alumina (Al_2O_3) and its antifouling research

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Abstract

Organic–inorganic composite membranes are formed by nano-sized alumina particles uniformly dispersed in the poly(vinylidene fluoride) solution (19% polymer weight). Membranes were prepared by phase inversion process and were characterized by ultrafiltration (UF) experiments in terms of water flux, molecular weight cut-off for the wet membranes. Contact angle between water and the membrane surface were measured by contact angle measurement in order to characterize the hydrophilicity changing of the membrane surface. The cross-sectional structures, porous dispersion in membranes surface and nanometer particles distribution in the membrane were examined by scanning electron microscopy (SEM) and transmission microscopy (TEM), respectively. The effect of nanometer Al_2O_3 particles concentration in the polymer dope on the permeation properties, membrane structures and antifouling performances were examined. The experimental results indicate that Al_2O_3–PVDF composite membranes exhibit significant differences in surface and intrinsic properties due to nanometer particles addition.

Keywords: Composite membrane; Poly(vinylidene fluoride); Nano-sized Al_2O_3 particles

1. Introduction

Ultrafiltration has been used extensively in many membrane separation processes, especially in wastewater treatment field such as oil–water separation [1–4]. The hydrophilicity of the membranes and its porous structure play an essential role in membrane separation processes. A good porous membrane used in these processes must have high permeability, good hydrophilicity and excellent chemical resistance to the feed streams. In order to obtain the high permeability, the high surface porosity and good pore structure of membranes are essential. Asymmetric membrane is the most ideal one for this object. Among all organic macromolecule polymer materials, PVDF is one of the excellent materials that can form asymmetric membranes [5,18]. PVDF-based membranes show outstanding oxidative, thermal and hydrolytic stability as well as good mechanical and film-forming properties. Thus, PVDF membranes are widely used in many ultrafiltration processes through various modifications.

There are many studies on improving the PVDF membrane performances. These studies include physical blending, chemical grafting and surface modifying. Blending of polymers presents the advantage of an easy preparation by the method of phase inversion. Nunes and Peinemann [6] reported asymmetric membranes for UF obtained from PVDF/PMMA without loss of retention. Pore size distribution showed a large increase in number of pores with sizes of 10–30 nm. The addition of PMMA also increases the size of finger-like cavities. Ochoa and Masuelli [7] made membranes with different degrees of hydrophlicity of PVDF and PMMA. A higher hydrophilic character with the increase of PMMA in the casting solution and the appearance of larger macrovoids in the porous substructure were found without a substantial modification of the selective surface structure. In addition to PMMA, other organic materials which can improve PVDF membrane properties are PMA (poly(methyacrylate)) [8,9], PVAc (poly(vinylacetate)) [10], CA (cellulose acetate) [11], etc. Although organic hydrophilic materials addition can

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improve some properties of membranes, it can also reduce membranes strength.

Studies of PVDF blending modification focus on inorganic materials blending recently. It has been demonstrated that the addition of the inorganic filler has led to an increase in the membrane permeability and a better control of membrane surface properties [12–16]. Inorganic materials that could be blended with PVDF include silica (SiO_2) [14], zirconium dioxide (ZrO_2) [15], and some small molecule inorganic salts such as lithium perchlorate ($LiClO_4$) [16]. A common point of these modifications is a higher proportion of inorganic materials addition. For SiO_2–PVDF, ZrO_2–PVDF and $LiClO_4$–PVDF, ratios of inorganic particles to PVDF are 20, 100, and 12.8%, respectively [14–16]. No any advantage is shown even for nano-sized particles SiO_2 [17]. The PVDF membranes morphology and membrane's elasticity have been affected significantly due to a mass of inorganic materials addition.

In this presentation, PVDF UF membranes are modified by inorganic nano-sized Al_2O_3 particles. This research aims at preparing Al_2O_3–PVDF composite membranes by phase-inversion method [18], which include only a small proportion of Al_2O_3 particles that can improve membrane performances effectively. The effect of Al_2O_3 particles concentration in the casting solution on membranes hydrophilicity, permeation flux, morphology, mechanical properties and antifouling performance is examined.

2. Experimental

2.1. Materials

The polyvinylidene fluoride used was a commercial product (FR904). Dimethylacetamide (DMAC, >99%, reagent) was used as the solvent. Alumina particles with nano-size of 10 nm were used as additive for PVDF solutions. Other additives used include hexad-sodium phosphate, polyvinylpyrrolidone (PVP), and a mixture of distilled water and ethanol was used as the non-solvents for the polymer precipitation.

2.2. Membrane preparation

Al_2O_3–PVDF composite membranes were made by phase-inversion method. Casting dopes were prepared by dissolving the PVDF in the solvent at room temperature and adding nano-sized Al_2O_3 particles and other additives to casting dopes under stirring. In order to obtain an optimal dispersion of the particles in polymer solutions, along with agitation for at least 24 h was necessary. Sometimes ultrasonic vibration was important method employed for obtaining a homogeneous suspension. Casting solutions were deposited in a no sun light place for one day for removing air bubbles from it.

An appropriate amount of the dope was dispersed uniformly on a glass plate and after a 30 s exposure period in air, it was immersed immediately in a bath which consisted of distilled water and ethanol. Two kinds of sheet membranes were laboratory prepared:

(a) without nano-sized Al_2O_3 particles;
(b) with nano-sized Al_2O_3 particles and surfactant hexad-sodium phosphate.

Different concentration Al_2O_3 particles (0–4%) of polymer dopes consisting of PVDF (19%, weight), DMAC (78%, weight), and additives were prepared. They were labeled as PVDF-0, PVDF-1, PVDF-2, PVDF-3, and PVDF-4, respectively. The formed membranes were washed with and immerged in distilled water until they were used as characterization samples.

2.3. Characterization of membrane

The formed membranes were characterized by the methods show below:

(1) The membrane permeation properties were tested in an ultrafiltration (UF) laboratory unit (effective area is 32.3 cm^2) fed with distilled water at different trans-membrane pressures (range from 0.1 to 0.4 MPa).

In the same unit fed with different molecular weight protein: cell pigment C (molecular weight 12,400), pepsin (molecular weight 35,000) and bovine serum albumin (molecular weight 67,000), respectively, to obtain molecular weight cut-off of membranes. When its rejection is more than 90% (weight), the protein's molecular weight was considered as molecular weight cut-off of the membrane.

(2) Membrane porosity was measured in the method of dry–wet weight.

(3) Contact angle between water and the membrane surface was measured in a contact angle measurement (DSA10, American, needlepoint size is1.5 mm): a water droplet is placed onto a flat homogeneous membrane surface and the contact angle of the droplet with the surface was

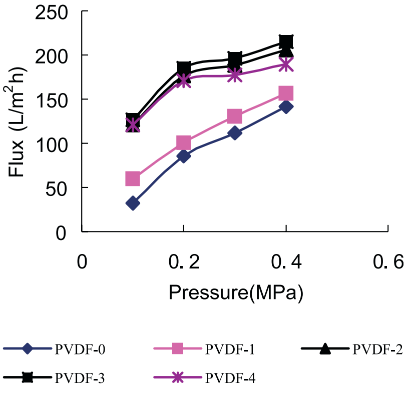


Fig. 1. Water fluxes of membranes prepared by dopes with different nano-sized Al_2O_3 particles.

Table 1
Membranes contact angle, pores rate, rejection and molecule weight cut-off

Membrane	PVDF-0	PVDF-1	PVDF-2	PVDF-3	PVDF-4
Contact angle (°)	83.64	67.87	57.42	58.62	58.97
Porosity (%)	54.99	54.72	55.31	53.09	55.82
Rejection (%)	95.50	96.31	96.5	97.05	96.45
Molecule weight cut-off	35,000	35,000	35,000	35,000	35,000

measured. The value was observed until there was no change in contact angle during the short measurement time.

(4) Tensile intensity and break elongate ratio of membranes were determined by a universal electronic strength measurement (W-56). Measurements were carried out in room temperature and a strain rate of 2 mm/min was employed [19].

(5) Porous dispersion of the membrane surface, the cross-sectional structures and nanometer particles distribution were examined by scanning electron microscopy (SEM, S-4700, Japan) and transmission electron microscopy (TEM, JEM-2000EX, Japan), respectively. Simples were prepared by fracturing membranes at liquid nitrogen temperature. All specimens were coated with a thin layer of gold before SEM observation.

(6) In order to observe membranes fouling condition, membranes were tested in a died-end ultrafiltration cup fed with oil–waste water from the oil field. The flux was decreasing with filtration time increasing due to membrane fouling. Species and quantities of contaminations on fouling membranes were analyzed by the uniting of gas chromatography and mass spectrum (GC-6890N/MS-5973N, American).

3. Results and discussion

3.1. Effect of adding nano-sized Al_2O_3 particles on membrane flux

Membrane flux was affected by the addition of nano-sized Al_2O_3 particles. Fig. 1 indicates that an increase of the Al_2O_3 concentration leads to an increase of the water permeate flux while this trend is not in evidence when nano-sized Al_2O_3 particles reached to some certain quantity. This can be interpreted by follows: PVDF is a hydrophobic polymer. Its hydrophilicity can be improved significantly due to the adding of nano-sized Al_2O_3 particles, which have many characteristics such as hydrophilic and bigger ratio surface areas, etc. Thus water fluxes are increased. However, casting drops consist of more amounts nano-sized Al_2O_3 particles, its flux cannot be more improved since, nano-sized Al_2O_3 particles reunited phenomena [20]. From economy and practicality, 2% (weight) of nano-sized particles in the casting solution are more properly.

It can also be seen from Fig. 1, water fluxes were enhanced with the pressure increasing for all membranes. This just is the peculiarity for asymmetric microfiltration and ultrafiltration membranes. Water fluxes can be improved through increasing driving force. But excessive driving force would increase running cost of facility and affect the membranes natural life. In this experiment, we would take 0.1 MPa as the transmembrane pressure. There is more than 100% increased in water flux of the membrane that consists of 2% (weight) Al_2O_3 particles at 0.1 MPa transmembrane pressure.

3.2. Contact angle, porosity, rejection and molecule weight cut-off of membranes

The contact angle is an important parameter in measuring of the surface hydrophilicity [21,22]. In general, membrane surface hydrophilicity is higher while its contact angle is smaller. It can be seen from Table 1, an increase of Al_2O_3 particles causes a decrease of the contact angle. But porosity, retention and molecule weight cut-off are not

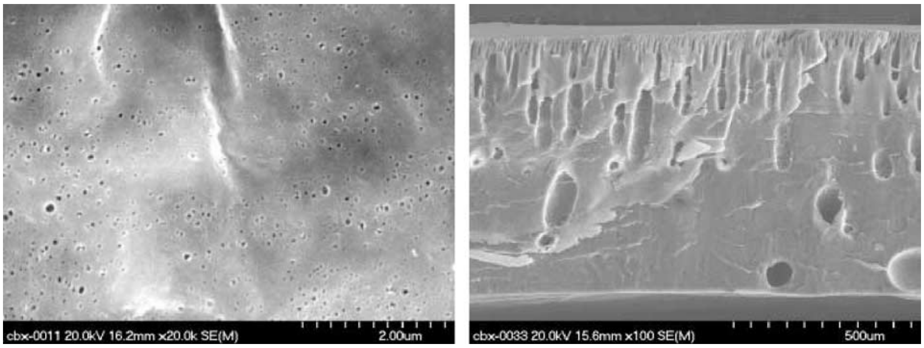


Fig. 2. SEM micrographs of the modified membranes surface and cross-section structures.

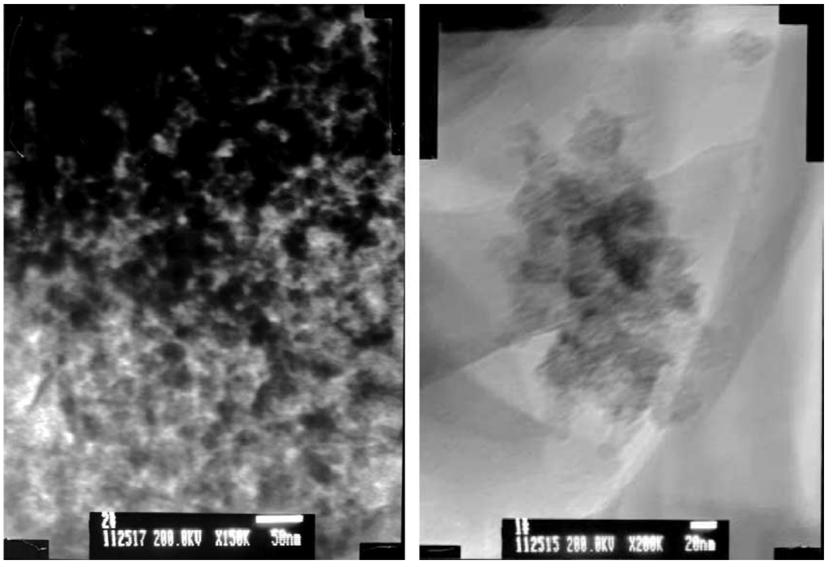


Fig. 3. TEM micrographs of nanometer particles distribution in the modified membrane.

effect by the Al_2O_3 particles. The results demonstrate that adding Al_2O_3 particles into PVDF polymer can improve its hydrophilicity, and not affect its pores sizes and numbers. An evidence behavior of composite membranes is flux increasing significantly.

3.3. Microstructures of membranes

Fig. 2 shows SEM micrographs of surface and cross-section structures of the modified membranes. It is apparent that the nano-sized pores (20–50 nm) are uniformly dispersed along the entire membrane surface and the cross-section structure of the composite membrane is typical asymmetric morphology. This indicates that the addition of nano-sized Al_2O_3 particulars cannot affect structures of surface and cross-section. Therefore, the mechanism of PVDF membrane formed is not altered by addition of inorganic nano-sized Al_2O_3.

Performances of modified membranes are influenced by the condition of nano-sized particulars distributing. Anion surfactant is used as dispersant in order to make inorganic particulars disperse in cast dopes uniformly. From Fig. 3, we can see nano-sized Al_2O_3 particulars are dispersed in the membrane as nano-sized grade (10–30 nm), which improved modified membranes hydrophilicity significantly. Above all, the composite membrane is not only keeping organic membranes traits but also improving its hydrophilicity, intensity and antifouling properties.

Table 2
Mechanical properties of membranes

Sample	Tensile intensity (N)	Break elongate ratio (%)
PVDF-0	13.2031	4.72
PVDF-1	18.3593	5.89
PVDF-2	19.9218	7.34
PVDF-3	20.2343	6.67
PVDF-4	20.5312	5.58

3.4. Mechanical properties

Tensile intensity and break elongate ratio of membranes are listed in Table 2. Both values of membranes are improved especially to tensile strength. Break elongate ratio is firstly increasing with the addition of nano-sized particles and it has a peak value when Al_2O_3 particles concentration is 2.0% (weight), and then declining with the Al_2O_3 particles concentration increasing. These behaviors indicate that adding appropriate amount of nano-sized Al_2O_3 particles into PVDF solution can improve the membrane mechanical properties. But excessive amount of inorganic Al_2O_3 particles in cast solution can cause the membrane elasticity decline, thus lead the membranes break elongate ratio decline. But for the membrane that consists of 2% (weight) Al_2O_3 particles, both tensile intensity and break elongate ratio values are heightened more than 50%.

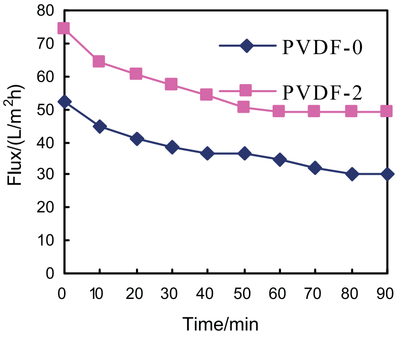
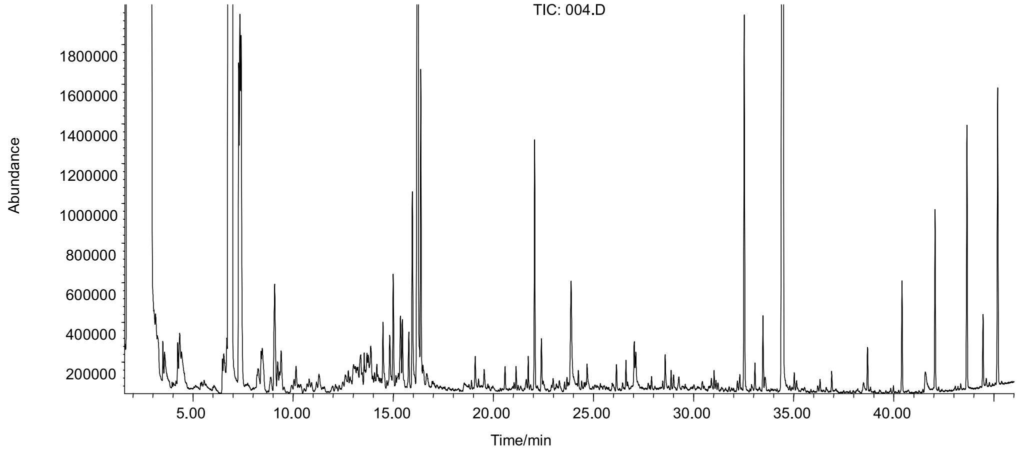
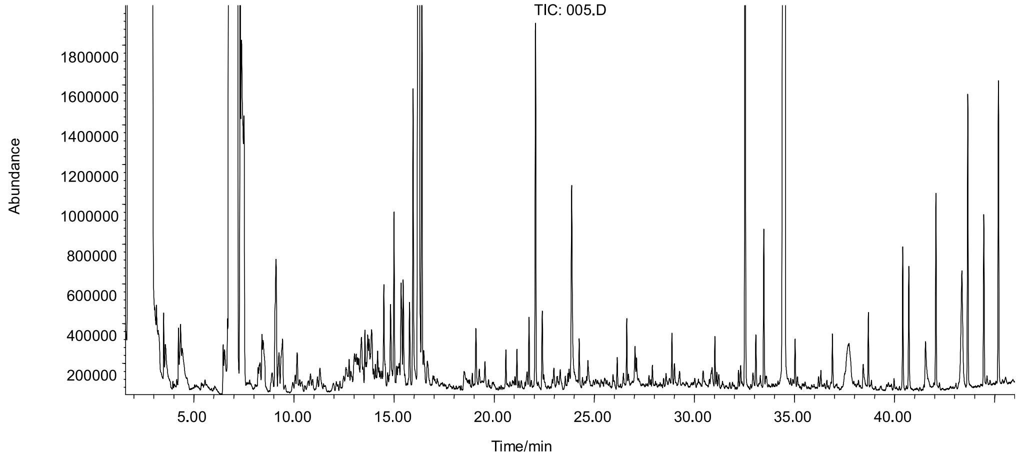


Fig. 4. Permeate flux decline with time for PVDF-0 and PVDF-2 membranes measured at 0.1 MPa transmembrane pressure.



PVDF-2



PVDF-0

Fig. 5. Gas chromatogram and mass spectra for membranes contaminations.

3.5. Antifouling performance

Membrane fouling is a complex phenomenon. The directly behave is permeate flux decline drastically. Reasons that cause the membrane fouling are very complex. Among of them, membranes hydrophilicity is an important factor that relates to the surface adsorption properties of the membrane, i.e. improving hydrophilicity of the membrane can reduce membrane fouling in some extent. From Fig. 4, permeate fluxes of membranes are declining with the increasing of filtration time and then no changing at a steady value for a long time. Flux declining ratio, defined as the flux of the membrane at the time of consistent flux divided by the initial flux of clear membrane, is 33.89% for PVDF-2 membrane, but is 42.31% for PVDF-0 membrane. From this we can see that antifouling performances of modified membranes are improved.

Oil–waste water ultrafiltration is running for 90 min and the value of flux is consistent, fouled membranes were washing with water and 0.1% OP-10 surfactant solution (PH = 10) for 10 min, respectively. Flux recoveries of membranes are listed in Table 2. Values of the table indicate that the flux recovery ratio, defined as the flux recovery value after washing divided by the initial flux value, of modified membrane PVDF-2 is always higher than that of unmodified membrane PVDF-0 with water and

Table 3
Flux recoveries of backwashing membranes

Membranes	Initial flux (L/m^{2}h)	Water washing		Surfactant washing	
		Flux (L/m^{2}h)	Flux recover ratio (%)	Flux (L/m^{2}h)	Flux recover ratio (%)
PVDF-0	52.02	46.06	88.5	50.23	96.6
PVDF-2	74.30	67.99	91.5	73.51	98.9

surfactant solution washing. The reason that causes this phenomenon is the hydrophilicity improvement for modified membranes and thus reducing contaminations adsorption potential of oil–waste water. Analyses uniting of gas chromatography and mass spectrum can prove this viewpoint (Fig. 5). Finding that about forty-four kinds of contaminations are adsorbed on the membrane PVDF-2, but about 68 kinds of contaminations are adsorbed on the membrane PVDF-0. From adsorption peak areas, modified membrane PVDF-2 is less 21.65% than unmodified membrane PVDF-0. It indicates that amounts of contaminations adsorbed on the modified membrane are reduced. Fig. 5 can also show this conclusion in qualitative from intensities and numbers of adsorption peak. All these are owed to hydrophilicity improvement of the modified membrane (Table 3).

4. Conclusions

Al_2O_3–PVDF composite membranes were synthesized by the phase-inversion process. The addition of the nano-sized Al_2O_3 particles did not affect membrane pore sizes and numbers, only by improving its surface hydrophilicity to improve many other properties of the membrane. The permeation flux increase of the membrane is attributed to surface hydrophilicity increase due to the hydrophilic inorganic nano-sized Al_2O_3 particles addition. Both tensile intensity and break elongate ratio values of the membrane are heightened more than 50% for the membrane that consists of 2% (weight) Al_2O_3 particles. The improvement of composite membranes hydrophilicity makes its antifouling performance increase. The flux-declining ratio of the modified membrane is less than that of the unmodified membrane. Flux recoveries of modified membranes are higher than that of unmodified ones, and amounts and kinds of contaminations adsorption are reduced.

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