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Preparation and characterizations of poly(vinylidene fluoride)/oxidized multi-wall carbon nanotube membranes with bi-continuous structure by thermally induced phase separation method

Hai-Peng Xu, Wan-Zhong Lang*, Xi Yan, Xuan Zhang, Ya-Jun Guo

The Education Ministry Key Laboratory of Resource Chemistry and Shanghai Key Laboratory of Rare Earth Functional Materials, Department of Chemistry and Chemical Engineering, Shanghai Normal University, 100 Guilin Road, Shanghai 200234, China

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ABSTRACT

Poly(vinylidene fluoride)/oxidized multi-wall carbon nanotube (PVDF/O-MWCNT) flat membranes with bi-continuous structures were successfully prepared via the thermally induced phase separation (TIPS) method. The effects of O-MWCNT content, PVDF concentration and quenching temperature on the membrane properties were systematically discussed. The results indicate that the membrane structure changes to a denser one and the pure water fluxes (PWFs) of the resultant membranes decline with the increase of O-MWCNT content. With the addition of O-MWCNTs from 0.0 to 0.6 wt%, the BSA rejections of the resultant PVDF/O-MWCNT membranes are improved dramatically. The highest BSA rejection attained is above 90.0%, implying that a novel PVDF/O-MWCNT ultrafiltration membrane is fabricated. The surface hydrophilicity and anti-fouling ability of the membranes are improved with the addition of O-MWCNTs. Furthermore, the mechanical properties of the resultant membranes are enhanced compared with the pristine PVDF membranes. This work demonstrates that O-MWCNTs play a critical role in determining the morphologies and performances of PVDF/O-MWCNT membranes prepared via the TIPS method.

1. Introduction

For its superior thermal and chemical stability, oxidation resistance, etc., PVDF is used as an ideal membrane material [1–4]. However, its hydrophobic nature often results in severe permeability decline. To overcome this shortcoming, numerous inorganic nano-fillers were used as membrane additives such as Al_2O_3 [5,6], ZnO_2 [7], SiO_2 [8], LiClO [9], ZrO_2 [10], and TiO_2 [11]. It was demonstrated that the addition of these fillers had positive effects on membrane permeability and morphology. For its high specific surface area, ease of functionalization, chemical stability and thermal conductance, multi-wall carbon nanotubes (MWCNTs) also attracted considerable attention in the membrane field [12]. Zhao et al. [13] successfully prepared PVDF/MWCNT membranes, and the blended membranes exhibited improved hydrophilicity, PWFs and higher bovine serum albumin (BSA) rejection. Ma et al. [14] investigated the effects of oxidized MWCNTs (O-MWCNTs) on PVDF membranes. They found that the oxygen-containing groups of O-MWCNTs played a critical role in determining the morphologies and performances of PVDF membranes. Zhang et al. [15] investigated the combined effects of graphene oxide (GO) and O-MWCNTs on the structure, permeation and anti-fouling ability of PVDF membranes. By changing the mass ratio of GO/OMWCNTs, the modified PVDF membranes showed a higher pore density and a lower contact angle. PWFs and anti-fouling ability of the membranes were also enhanced.

In previous studies, the PVDF membranes modified by embedding MWCNTs were mainly prepared through non-solvent induced phase separation (NIPS) which referred to numerous parameters, and caused the preparation process to be complicated and uncontrollable [1,16,17]. In recent years, the thermally induced phase separation (TIPS) method has been considered to be reliable and is widely used due to the better properties of the resultant membranes compared with those produced by NIPS [18,19]. Table 1 summarizes the recent studies on the PVDF and some other polymeric membranes prepared via TIPS as well as their permeation and rejection properties from 2000 to 2013. Many factors determining the performances of PVDF membranes in the TIPS process were studied in detail including inorganic [20,21], organic [22] and polymer additives [23–25], diluents [19,26–31], and the preparation process [32–34]. Besides PVDF, there were some other polymeric membranes (PVB [35–37], IPP [38,39], PP [40,41] and so on [42,43]) also prepared via TIPS. As can be seen from Table 1, up to now, there have been no studies

* Corresponding author. Tel./fax: +86 21 64321951.
E-mail address: wzlang@shnu.edu.cn (W.-Z. Lang).

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Table 1
The published studies about PVDF and some other polymeric membranes via TIPS from 2000 to 2013.

Authors	Polymer	Geometry	Year	MF/UF	Pore size (μm)	Rejection (solutes)	PWFs(Max) L M^{-2} H^{-1} bar^{-1}
Cui [19]	PVDF	Flat sheet	2013	MF	> 0.16	–	< 3500
Cui [19]	PVDF	Hollow fiber	2013	MF	> 0.12	–	< 1200
Shi [20]	PVDF	Flat sheet	2013	MF	–	< 15% (BSA)	< 140
Li [21]	PVDF	Hollow fiber	2013	–	–	–	< 280
Liu [22]	PVDF	Flat sheet	2013	MF–UF	> 0.085	–	< 470
Rajabzadeh [23]	PVDF	Hollow fiber	2012	–	–	< 80% (BSA)	< 200
Li [24]	PVDF/ UHMWPE	Hollow fiber	2011	MF	> 0.3	–	< 310
Ghasem [25]	PVDF	Hollow fiber	2011	MF	> 4.47	–	< 10
Qiu [26]	PVB	Hollow fiber	2010	–		PS particles (102 nm) < 90%	< 2
Liu [27]	PVDF	Flat sheet	2010	UF	R_m (0.012–0.082)		< 300
Cui [28]	PVDF	Hollow fiber	2010	–	–	–	< 150
Rajabzadeh [29]	PVDF/PMMA	Hollow fiber	2009	–	–	–	< 200
Lu [30]	PVDF	Flat sheet	2009	MF	> 0.3 Mpa	–	< 350
Yang [31]	PVDF	Flat sheet	2008	–	> 0.089	–	–
Rajabzadeh [32]	PVDF	Hollow fiber	2008	–	–	PS particles (20 nm) ≤ 95%	< 800
Qiu [33]	PVB	Hollow fiber	2008	MF	–	PS particles (102 nm) < 98%	< 450
Ji [34]	PVDF	Hollow fiber	2008	MF	> 0.12	Carbon ink (> 0.16 nm)	< 550
Ji [35]	PVDF	Flat sheet	2007	MF	> 1	–	–
Yang [36]	IPP	Hollow fiber	2006	–	–	–	< 400
Yang [37]	IPP	Hollow fiber	2006	MF	> 0.17	–	< 450
Fu [38]	PVB/EVOH	Hollow fiber	2006	–	–	PS particles (50 nm) < 50%	< 1100
Yave [39]	sPP/IPP	Flat sheet	2005	MF	> 0.4	–	< 2500
Fu [40]	PVB	Hollow fiber	2005	–	–	PS particles (50 nm) < 30%	< 360
Shang [41]	EVOH	Hollow fiber	2003	UF	–	PS particles (100 nm) ≈ 100%	< 180
Matsuyama [42]	HDPE	Hollow fiber	2003	MF	> 0.2	–	< 360
Matsuyama [43]	PP	Flat sheet	2000	MF	> 0.1	PS particles (100 nm) ≈ 0%	< 650

investigating the influences of MWCNTs on the performances of PVDF/O-MWCNT membranes via the TIPS process. Also, the synthesized membranes were mainly categorized as microfiltration membranes according to the rejection data.

In this work, the PVDF/O-MWCNT flat sheet membranes were successfully fabricated via the TIPS method. The effects of O-MWCNT content, PVDF concentration and quenching temperature on the membrane properties, such as morphology, hydrophilicity, filtration and anti-fouling ability, and mechanical properties were discussed in detail.

2. Experimental

2.1. Materials

PVDF in powder form was supplied by Shanghai 3F New Material Co. Ltd. (China). Raw multi-wall carbon nanotubes (R-MWCNTs, diameter 10–20 nm, length 10–15 μm, purity > 97.0 wt %) were purchased from Shenzhen Nanotech Port Co. Ltd. (China). Dibutyl phthalate (DBP), hydrochloric acid(HCl), nitric acid (HNO_3), potassium bromide (KBr) and ethanol were provided by Shanghai Chemical Agent Co. Ltd. (China). Deionized water (DI) was produced by a reverse osmosis (RO) system. BSA (M_W=67,000) was purchased from Shanghai Bio Co. Ltd. (China). None of the reagents were further purified before used.

2.2. Preparation of oxidized MWCNTs (O-MWCNTs)

The nitric acid vapor-oxidation method was adopted to prepare O-MWCNTs. Firstly, to remove the impurities (metallic catalyst particles and amorphous carbon), 10 g of MWCNTs was soaked in 0.5 M HCl solution at room temperature for at least 12 h. Then, the treated MWCNTs (T-MWCNTs) were filtered and washed with DI water till neutral, and dried in a vacuum oven at 80 °C. To introduce carboxy groups, 1 g T-MWCNTs and 10 ml concentrated nitric acid were put in a self-made device (illustrated in Fig. 1). Then, the device was heated to 160 °C in an oven for 6 h. The O-MWCNTs were sequentially filtered and washed with DI water and ethanol to remove residual acid. Finally, the O-MWCNTs were dried at 80 °C in a vacuum oven for 12 h.

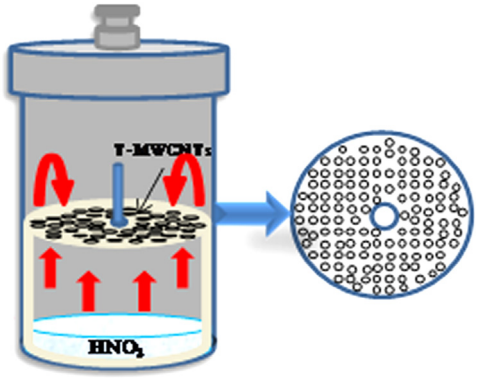

Fig. 1. The device for the functionalization of MWCNTs.

2.3. Characterizations of O-MWCNTs

The Fourier-transform infrared spectra (FTIR ElectronCorp Nicolet 380) of the obtained O-MWCNTs were collected to identify oxygen-containing groups in the samples.

The thermal stability of R-MWCNTs and O-MWCNTs was characterized by a thermo-gravimetric analyzer (TGA) in nitrogen atmosphere from room temperature to 800 °C at the rate of 10 °C/min. The weight loss ratio was named as R_L.

2.4. Membrane preparation

The PVDF/O-MWCNT membranes were prepared by the TIPS method with DBP as the diluent and tap water as the quenching bath. Firstly, different amounts of O-MWCNTs and DBP diluent were mixed and intensively stirred with the assistance of ultrasonic for 20 min. Different amounts of PVDF (dried at 70 °C before