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Developing nanofiltration membrane based on microporous poly(tetrafluoroethylene) substrates by bi-stretching process

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ABSTRACT

A thin film composite (TFC) nanofiltration membrane was fabricated through interfacial polymerization on microporous poly(tetrafluoroethylene) (PTFE) substrates, which were fabricated by bi-stretching process (longitudinal and transverse stretching). Multilayers were formed on PTFE substrate via physical twining and chemical linkage. Impacts of bi-stretching ratios on separation properties of TFC nanofiltration membrane were deeply investigated. Results indicate that the increase of longitudinal stretching ratio increased the length of fibrils and induced larger pore sizes and porosities, which resulted in lower values of rejection and higher permeate flux. However, the increase of transverse stretching ratio induced that the pore sizes declined and the porosities increased, which may be due to interlaced fibrils. Accordingly, it induced higher values of rejection and permeate flux. The obtained TFC nanofiltration membrane exhibited good acid stability (over 30 days) and high stability on long term (over 90 days). It could be potentially employed in nanofiltration process.

1. Introduction

Recently, water pollution becomes one of the critical concerns. Membrane separation is a promising method for wastewater treatment. Nanofiltration (NF) process is increasingly attracting worldwide research interest, which has found widespread industrial applications in such areas as softening, wastewater treatment, retention of dyes and removal of organic solvents [1–6].

TFC nanofiltration membrane often includes a microporous substrate and a skin layer. The skin layer is dense and thin to ensure effective separation and high flux. One of the most effective methods is interfacial polymerization. The performance of the skin layer greatly depends on preparation parameters [7–11]. The microporous substrate is also important except for the skin layer. However, few reports on the effect of substrate properties are available in the literature. Singh et al. presented a reverse osmosis membrane with different polysulfone substrates [12]. Ghosh and Hoek studied the formation of composite membranes with polysulfone substrates [13]. Ismail et al. deeply revealed the effect of polysulfone substrate characteristics on formation of TFC naofiltration membrane, which found that it portrayed a major role in the changes of the skin layer [14]. It is believed that the substrate characteristics may influence the morphology and performance of TFC nanofiltration membrane [12–15].

Recently, polysulfone and polyethersulfone ultrafiltration membranes are well accepted as the microporous substrates [12–18]. In addition, TFC nanofiltration membrane is also fabricated with other microporous substrates, such as polypropylene, polyacrylonitrile, polyvinylidenefluoride and poly(phthalazione ether nitrile ketone) [10,19–22]. However, some drawbacks occur when they are employed as the substrates [7]. In terms of this, chemically and thermally stable substrates are urgently needed.

Polytetrafluoroethylene (PTFE) attracts great attention because it is highly chemical resistant, thermal stable and mechanical resistant. Our research group has been researching on PTFE membranes over decades [23]. Only longitudinal stretching process could increase the porosities of PTFE membranes. The pore sizes also increased. However, bi-stretching process could induce that the pore sizes decline and the porosities increase, which would be very helpful for separation process. Recently, few reports on PTFE flat-sheet membranes by bi-stretching process were available. In addition, up to now, PTFE membranes are general microfiltration membranes. The minimum pore size is generally ~0.1 μm, which is larger than that of polysulfone or polyethersulfone ultrafiltration membrane. Furthermore, PTFE membranes are highly hydrophobic, which could not be directly employed as the substrate. Several chemical modifications (i.e. plasma) for hydrophilicity were employed, which would inevitably destroy its intrinsic structure in some extent [24].

In this study, microporous PTFE substrates were fabricated by bi-

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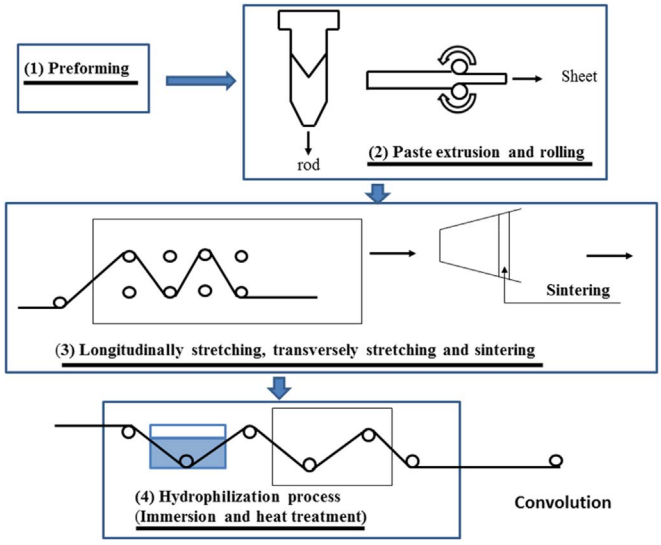

Fig. 1. Flow chart of fabrication of hydrophilic PTFE flat-sheet substrates.

stretching (longitudinal stretching and transverse stretching) process, which would become highly hydrophilic through a simple physical modification. Subsequently, interfacial polymerization on hydrophilic PTFE substrates was employed to fabricate TFC nanofiltration membrane. The interactions between different layers on the PTFE substrate were studied. Impacts of bi-stretching ratios (longitudinal stretching ratio and transverse stretching ratio) on separation properties of TFC nanofiltration membrane were deeply investigated. Furthermore, stability tests of TFC nanofiltration membrane (the acid stability and stability on long term) were performed. It is expected that these findings could provide more insight in fabrication of TFC nanofiltration membrane with microporous PTFE substrates.

2. Experimental section

2.1. Materials

Amine monomer piperazine (PIP, 99%), polyacrylic acid (PAA, 98%), trimesoyl chloride (TMC, 98%), sulfuric acid (H_2SO_4, 98%), hexane (99%), methylene blue, conger red and neutral red were supplied by Shanghai Aladdin Chemicals Co., Ltd. Sodium sulfate (Na_2SO_4), magnesium sulfate ($MgSO_4$), sodium chloride (NaCl) and magnesium chloride ($MgCl_2$) were supplied by Hangzhou Gaojing Chemicals Co., Ltd. Triethylamine (TEA, 98%) was supplied by Tianjin Yongda Chemicals Co., Ltd. Sodium dodecyl sulfate (SDS, 99%) was supplied by Shanghai Sibaiquan Chemicals Co., Ltd. Polyethylene glycol (PEG) was supplied by Tianjin Kerml Chemicals Co., Ltd. Aziridine crosslinking agent was supplied by Guangzhou Zhuoneng Chemicals Co., Ltd. PTFE powders were supplied by Quzhou Juhua Fluoroproducts Co. Ltd.

2.2. Fabrication of hydrophilic PTFE flat-sheet substrates

1) Preforming:

The preparation process in detailed is presented in Fig. 1. The mixture of PTFE powders and lubricant (Isoparl G, 20 wt%) was kept at 30 °C over 24 h. Subsequently, the mixture was pressurized to become a cylindrical billet.

2) Paste extrusion and rolling:

The cylindrical billet was extruded into a rod. Then, rolling process in one direction was followed, which induced a sheet with a thickness of 120 μm.

3) Stretching and sintering:

Longitudinal stretching process was initially performed in an oven. Different longitudinal stretching ratios were employed (100%, 200%, 300%), which is defined in Eq. (1). Simultaneously, the lubricant was removed. Subsequently, transverse stretching process was carried out in an oven. The transverse stretching ratios (150%, 250%) were listed in Table 1. Final process was sintering at ~360 °C over 1 min. As a result, PTFE flat-sheet substrates would be fabricated (designated as M1-M5).

$$Stretching ratio = \frac{L - L_0}{L_0} \times 100\% \quad (1)$$

Herein, L is the length of PTFE flat-sheet substrate after stretching. L_0 is the length of PTFE flat-sheet substrate before stretching.

4) Hydrophilization process:

PTFE flat-sheet substrates were all hydrophobic (As shown in Table 1), which would be immersed in a hydrophilic compound (the mixture of polyacrylic acid and aziridine crosslinking agent) over several minutes. PTFE flat-sheet substrates would be wetted by the hydrophilic compound.

The next process is heat treatment in an oven lower than 100 °C. Partial crosslinking reaction would engender between polyacrylic acid and aziridine crosslinking agent during this period, which is shown in Eq. (2). As a result, the hydrophilic PTFE substrates were produced, which can be seen in Table 1. Water drip was absorbed by the surface of hydrophilic PTFE substrates over ~7 s (from 12 s to 19 s) during contact angle measurement. The corresponding video is shown in **Supplementary data**.

Supplementary material related to this article can be found online at http://dx.doi.org/10.1016/j.memsci.2016.11.030.

Table 1
The parameters of PTFE flat-sheet substrates.

Sample	M1	M2	M3	M4	M5
Longitudinal stretching ratio	100%	200%	300%	300%	300%
Transverse stretching ratio	0	0	0	150%	250%
Contact angle, °	134.8	135.1	139.8	136.3	136.7
Contact angle (hydrophilic), °	0	0	0	0	0