Journal of Membrane Science 509 (2016) 94–104

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Microporous PVDF membranes *via* thermally induced phase separation (TIPS) and stretching methods

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ARTICLE INFO

Article history:
Received 7 December 2015
Received in revised form
6 February 2016
Accepted 21 February 2016
Available online 24 February 2016

Keywords:
PVDF membrane
Green solvent
TIPS
Stretching

ABSTRACT

Microporous polyvinylidene difluoride (PVDF) hollow fiber membranes were fabricated *via* a thermally-induced phase separation (TIPS) method using an environmental-friendly hydrophobic solvent, acetyl tributyl citrate (ATBC, tradename *Citroflex® A4*). To maximize membrane tensile strength, the TIPS method was fully utilized by spinning fibers with high polymer content. It was observed that the fiber quality was significantly affected by the dope and bore flow rates and compositions, and an appropriate spinning range was established. The prepared membranes were subsequently stretched to tune the porosity, mean pore size, permeability, tensile strength, and fiber strain. A design of experiment (DOE) analysis was conducted using a 3-factor quadratic model to optimize the stretching conditions and to understand the effects of the parameters and interactions thereof. The permeability of the stretched membranes improved by a factor of 35 (15.1–538 L m^{-2} h^{-1} bar^{-1}), and the tensile strength increased from 7.2 MPa to 8.4 MPa at the expense of the fiber strain. The DOE analysis revealed that the stretching ratio positively affects the permeability and porosity but decreases the fiber strain. On the other hand, it was determined that the stretching temperature positively influences the permeability and fiber strength. The stretched membranes exceeded the PVDF performance upper bound prepared by the TIPS method. The membranes were primarily in the α-phase polymorph, and stretching the fibers up to 40% at 90 °C did not induce any detectable β-phase crystals. The proposed preparation method offers a feasible and sustainable alternative to fabricate hollow fibers membranes with high tensile strength and high permeability.

1. Introduction

The field of membrane technology has expanded tremendously in the past few decades, with the market size expected to reach $28 billion in 2018 [1]. Membrane technology is now a well-accepted unit operation in various industries ranging from water treatment [2], food and dairy industries [3], battery separators [4], gas separation [5], and pharmaceutical industries [6,7]. Among the membrane fields, approximately 50% of the current applications require microporous membranes in areas including microfiltration (MF), ultrafiltration (UF), membrane bioreactors (MBR), and blood dialysis (*e.g.*, hemodialysis) applications [8]. In addition, the demand is increasing with new emerging applications such as membrane distillation (MD) and membrane crystallization (MCr) which require hydrophobic microporous membranes [9,10]. To maximize the productivity of the aforementioned applications, microporous membranes need to be fabricated with high mechanical and chemical stabilities, high porosity, narrow pore size distribution, and high pore connectivity. Furthermore, the fabrication materials and methods need to be affordable and environmentally sustainable.

Polymeric membranes can be fabricated using several different methods, including the non-solvent induced phase separation (NIPS), thermally induced phase separation (TIPS), electrospinning, and melt-spinning (MS) methods [11]. Among the reported methods, the NIPS method is widely used in membrane technology to fabricate a variety of membranes for applications including reverse osmosis (RO), gas separation, pervaporation, and MF/UF.

On the other hand, the TIPS method is more specialized for the

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http://dx.doi.org/10.1016/j.memsci.2016.02.050

fabrication of microporous membranes with a narrow pore size distribution, high porosity, and unique morphology [12,13]. In a typical TIPS process, a dope solution is prepared by dissolving a polymer of interest in a high-boiling point solvent at an elevated temperature, typically above the crystallization temperature (T_c) of the dope solution. The dope is then cast into a flat-sheet or hollow fiber form, followed by a cooling step at a controlled rate to induce phase inversion with subsequent solvent removal. In contrast to the NIPS method which is a ternary system (polymer, solvent, and nonsolvent), the TIPS method is typically a binary system composed of a polymer and solvent. Hence, the TIPS method offers higher reproducibility with a very low tendency for defect formation [13], which is of critical importance in most membrane applications.

Although membrane technology is widely recognized as a green process and a key technology for process intensification, the membrane fabrication process itself is far from being green and sustainable [14]. For instance, to prepare membranes using NIPS, significant volumes of harmful solvents such as DMF, NMP, and DMAc are commonly used [15]. Similarly, the TIPS method conventionally employs toxic phthalate-based solvents like dibutyl phthalate (DBP), diethyl phthalate (DEP), and dioctyl phthalate (DOP) [16–21]. Such solvents are known to be highly ecotoxic as they can bioaccumulate [22]. Environmental regulations around the world, particularly in the US and Europe, are becoming increasingly more stringent and such solvents need to be replaced with greener alternatives [23]. In fact, the use of DMF is highly discouraged in Europe [23] and phthalate-based solvents have been banned in the cosmetic industry [24].

Hence, recent membrane research has been focused on developing greener alternatives to fabricate polymeric membranes with improved performance [25,26] or to extract the toxic solvents after membrane fabrication [27]. Notably, although the criteria for the TIPS solvent are stricter, the TIPS method offers a wider selection of potential solvents because the dope is prepared at higher temperatures (hence a higher solubility of the polymer) [15].

Apart from the green requirements, the solvent hydrophobicity is also an important parameter. When preparing TIPS hollow fiber membranes, water is universally used as the quench media. Hence, when a hydrophilic TIPS solvent is used (high miscibility with water), a NIPS effect occurs on the surface that usually results in a dense skin layer. For instance, green solvents like γ-butyrolactone (GBL) [28], and Rhodiasolv PolarClean® [26] have been employed as TIPS solvents but dense skin layers have been observed with low flux. This unique phenomenon is now referred to as the N-TIPS method and deserves a separate attention [29–31]. However, for the preparation of microporous membranes, such a dense skin layer needs to be avoided. On the other hand, typical hydrophobic solvents widely used for the TIPS process are mostly phthalate-based, such as DBP and DOP [16,17]. These solvents are not environmentally friendly and require special precautions when handled, as they can bioaccumulate. It is unlikely that membranes prepared using such solvents would be approved for hemodiafiltration applications, which is the largest market for microporous membranes [32].

A recently identified and promising TIPS solvent is acetyl tributyl citrate (ATBC, tradename *Citroflex® A4*) [33,34]. This solvent has no reported health hazards (rated as 0 in MSDS), as it is typically employed as a plasticizer for pharmaceutical coatings and food packaging. In addition, ATBC is much more environmentally friendly compared to the phthalate-based solvents and more importantly, is not miscible with water. Hence, this solvent meets all of the necessary requirements as a TIPS solvent to fabricate microporous hollow fiber membranes.

Finally, one of the key requirements for membranes, often overlooked and even underestimated, is strong mechanical properties. For membranes to be used in real applications, a reasonable mechanical property is necessary for the membranes to be fabricated into modules such as spiral wound or hollow fiber modules. In addition, the membranes need to be strong and ductile enough to withstand tough operating conditions. For example, MBR processes require membranes with strong tensile strength and high elongation in order to withstand turbulent aeration and vibration conditions for prolonged periods.

It is well known that the membrane mechanical properties can vary significantly depending on the fabrication conditions. Two of the common methods to improve the mechanical properties of membranes are: (1) increasing the polymer content in the dope [35], and (2) using inorganic additives to prepare nanocomposite membranes [20]. As expected, improving the mechanical properties comes with a classical tradeoff of lower permeability, as is evident in the graphical abstract of this work. Notably, as mentioned by Lee et al. [28], the TIPS method is particularly suited towards employing the first method because the polymer solubility is much higher at elevated temperatures, allowing for a higher concentration dope to be prepared.

One of the practical methods to enhance the membrane permeability in fabrication of microfiltration membranes is to employ stretching [25,36]. Stretching method has been widely applied for preparation of microporous polypropylene (PP) and polytetrafluoroethylene (PTFE) membranes [37–40]. Generally, a stretching step is included as a post-treatment of extruded polymer films to form pores, or to enlarge pores. One of the critical aspects in stretching is to first induce row-nucleated lamellar structure prior to stretching, as it helps to concentrate stress at the phase interfaces to form pores. [41,42] It is known that inducing such row-nucleated lamellar structure is a function of polymer intrinsic properties as well as the processing parameters; and one of the most effective methods is to crystallize the polymer under high stress, and hence extrusion with high draw ratio is often employed to induce row-nucleated lamellar structure [43]. Another way is to quench the polymer film at a fast rate [42], which is more suitable method in the TIPS process. Stretching has also been actively applied to improve the permeability and mechanical properties of microporous PVDF membranes [25,36].

Our preliminary results have shown that the mechanical properties of PVDF/ATBC membranes were relatively weak [33,34]. Hence, in this work, we first prepared PVDF/ATBC hollow fiber membranes with high mechanical properties using TIPS. Then, in order to improve the permeability of the membranes, we investigated a stretching method using a Design of Experiment (DOE) analysis to maximize both the mechanical and permeability of the fiber membranes. The effects of the stretching temperature, stretching ratio, and holding time (relaxation) on the fiber permeability, tensile strength, porosity, and pore size, were statistically analyzed and interpreted.

2. Experimental

2.1. Materials

All of the employed solvents, except ATBC, were of analytical grade and purchased from Daechun Chemicals (Yeosu, South Korea). ATBC was purchased from Tokyo Chemical Industries Ltd. (Tokyo, Japan). PVDF (Solef® 6010) was kindly supplied by Solvay Specialty Polymers (Bollate, Italy).

2.2. Phase diagram

The crystallization temperatures of polymer dope solutions were measured using a differential scanning calorimeter (DSC Q20, TA Instruments, New Castle, Delaware, USA). Homogeneous PVDF/