



Preparation and characterization of novel poly(vinylidene fluoride) membranes using self-assembled dibenzylidene sorbitol for membrane distillation



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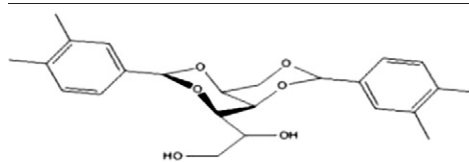
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HIGHLIGHTS

- Vapor-induced phase separation with a dry/wet process was used to produce membranes.
- DMDBS molecules self-assembled into nanofibrils outside the PVDF membranes.
- DMDBS nanofibrils acted as reinforcing materials to enhance the PVDF membranes.

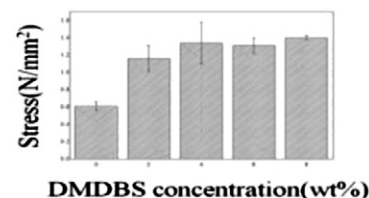
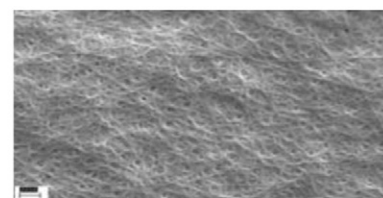
GRAPHICAL ABSTRACT



DMDBS(0~8wt%)

+

PVDF



ARTICLE INFO

Article history:

Received 10 July 2013

Received in revised form 14 October 2013

Accepted 18 October 2013

Available online 9 November 2013

Keywords:

Poly(vinylidene fluoride)

Self-assembly

Dibenzylidene sorbitol

Composite membranes

Reinforcing materials

Membrane distillation

ABSTRACT

We proposed a method for the preparation of novel poly(vinylidene fluoride) (PVDF) membranes with self-assembled 1,3:2,4-di(3,4-dimethylbenzylidene) sorbitol (DMDBS). The vapor-induced phase separation (VIPS) method with a dry/wet process was used to produce DMDBS/PVDF composite membranes. The resulting membranes exhibited the coexistence of PVDF cellular pores and crystalline particles. The DMDBS molecules self-assembled into nanofibril structures, and a large number of nanofibrils were found on the surfaces and in the cross-sections of the prepared membranes. The DMDBS nanofibril networks in the PVDF matrix acted as reinforcing materials that enhance the hardness and stiffness of the membranes. Moreover, because of the entangled DMDBS networks, a greater strain was required to induce sample failure; therefore, the ductility of the membranes increased with increasing amounts of DMDBS. In addition, in a membrane distillation process, our composite membranes exhibited a good permeate flux that was comparable to that of commercial PVDF membranes.

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1. Introduction

Membrane distillation (MD) has attracted the interests of academic and scientific studies in the last decades [1–3]. This process involves the thermally driven transport of vapor through porous, hydrophobic

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membranes. The driving force in the process is the difference in the vapor pressure induced between both membrane sides. Direct contact membrane distillation (DCMD), in which heated feeds and cold permeate water streams are in direct contact with the membranes and thus lead to simpler MD systems, is the most widely used method [4]. Therefore, porous membranes with excellent mechanical properties and hydrophobicity are necessary to ensure a high water permeate flux.

Poly(vinylidene fluoride) (PVDF) is a hydrophobic, chemically inert, engineered plastic. It is widely used for the production of porous membranes for microfiltration, pervaporation, and membrane distillation [5–8]. These porous membranes are usually prepared by phase inversion methods, such as thermally-induced phase separation, dry process, wet process, dry/wet process, and vapor-induced phase separation [5–10]. The vapor-induced phase separation method is similar to the wet process method. The non-solvent is introduced by the vapor, and the absorption by the polymer solution induces the phase separation. The dry/wet process combines the dry and wet processes. The solvent evaporation process causes the phase separation, and the final structure is formed after the solvent/non-solvent exchange. In this study, a vapor-induced phase separation involving the dry/wet process was used to produce PVDF membranes without macrovoids for application in the DCMD process.

Some additives or fillers were used to improve the hydrophobicity or mechanical properties of porous PVDF membranes [11–20]. PVDF was blended with some organic, hydrophilic polymers, such as polyvinylpyrrolidone (PVP) and poly(methyl methacrylate) (PMMA). These polymers can influence the solvent/nonsolvent exchange velocity and promote the formation of porous structures. As a consequence, these polymers enhance the water permeation performance, although the mechanical properties of the membrane are usually reduced [11,12]. Recently, inorganic fillers, such as TiO₂, SiO₂, and Al₂O₃, have been added to improve the mechanical properties of PVDF membranes [13–16]. Some disadvantages, such as high cost and non-uniform dispersion, need to be addressed.

1,3:2,4-Di(3,4-dimethylbenzylidene) sorbitol (DMDBS) is an amphiphilic molecule with two hydrophobic phenyl groups and two hydrophilic hydroxyl groups. The chemical structure is shown in Fig. 1. Other dibenzylidene sorbitol derivatives include 1,3:2,4-dibenzylidenesorbitol (DBS), 1,3:2,4-bis(p-methylbenzylidene) sorbitol (MDBS), and 1,3:2,4-di(p-chlorobenzylidene) sorbitol (Cl-DBS). A low concentration of these dibenzylidene sorbitol derivatives can self-assemble into 3-D nanofibrillar networks in organic solvents and liquid polymers [21–23]. The average diameter of these nanofibrils, as determined by microscopy, is approximately 10–20 nm. For industrial applications, these sorbitol derivatives are largely used as nucleating agents to change the nucleation rates or optical properties of poly(ethylene) and poly(propylene) [24–26]. In our previous study, the mechanical properties of polymers, such as polystyrene (PS), were enhanced by the addition of DBS because the cross-linked networks of DBS nanofibrils acted as reinforcing materials [27].

In brief, the flux enhancement for DCMD process is still very important [17], and membranes with high mechanical properties were thus needed to endure enhanced flux. DMDBS is an inexpensive additive and has been used as a reinforcing material in some polymers [27,28]. Therefore, the objective of this study is to use this most widely used sorbitol derivative as an additive to improve the structures and properties of PVDF membranes for membrane distillation. This is to our knowledge the first paper using sorbitol derivatives to prepare porous membranes. Our results show that the addition of DMDBS improves the porosity (due to its hydroxyl groups) and mechanical properties (due to its 3-D network structures) of PVDF membranes.

Because of the polymorphism, PVDF is used not only in the membrane distillation process but also in a wide range of applications, such as in supercapacitors, transducers, actuators, and batteries [29–31]. The crystal structure of the PVDF membrane that we

prepared has a β -crystal structure, which can be used for pyroelectric and piezoelectric applications. However, the mechanical properties of PVDF still need to be improved; thus, modifications to PVDF warrant further research. Our results demonstrate that the presence of DMDBS clearly improved the mechanical properties of PVDF. Therefore, our novel DMDBS/PVDF composites may be useful for these applications.

2. Experimental section

2.1. Materials

Poly(vinylidene fluoride) (Hylar 5000 HP) was obtained from Solvay Solexis. 1,3:2,4-Di(3,4-dimethylbenzylidene) sorbitol (Millithix 925s) was purchased from Milliken Chemicals. N,N-Dimethylacetamide (DMAc) was of reagent grade and was purchased from Tedia. Industrial-grade 2-propanol (IPA) and hexane were obtained from ECHO Chemical Company. Deionized water was used as the precipitation bath.

2.2. Sample preparation

PVDF and different amounts of DMDBS were dissolved in DMAc to obtain a 20-wt.% solution. These solutions were cast on a glass plate with a thickness of 250 μ m. The resultant casting films were exposed to water vapor (humid air) at 22 ± 1 °C with a relative humidity of 70 ± 2 for 10 min. The films were then immersed in a water bath for 24 h at room temperature. The newly formed membranes were then washed with IPA and hexane to exchange the residual water in the membranes. The membranes were then dried in a vacuum oven. It should be noted that when the DMDBS amount was increased to 9 wt.%, DMDBS did not dissolve in solvents completely. Thus, in this study, DMDBS concentrations of 0 to 8 wt.% were chosen for the following investigations. The percentage of DMDBS additive is based on the same PVDF concentration.

2.3. Scanning electron microscopy (SEM)

The microstructures of PVDF membranes with different DMDBS amounts were observed using a Leo-1530 field emission scanning electron microscope. The vacuum-dried membranes were directly used for the SEM experiments. All of the samples were sputtered with gold. The cross-section of the membranes was obtained by fracturing the membranes in liquid nitrogen.

2.4. Porosity

The porosities of the PVDF membranes with different DMDBS amounts were determined by the following equation [32,33]:

$$\text{Porosity}(\%) = \left(\frac{V_m - V_p}{V_m} \right) \times 100 \quad (1)$$

where V_m is the bulk volume of the membrane and V_p is the volume of the polymer. V_m was obtained by multiplying the membrane area by its thickness. V_p was calculated by dividing the weight of the membrane by the density of the PVDF polymer, which is 1.75 g/cm³.

2.5. Differential scanning calorimetry (DSC)

The thermal properties of PVDF membranes with different DMDBS amounts were measured using a Perkin Elmer Pyris Diamond differential scanning calorimeter. The DSC scan was performed under nitrogen atmosphere. The samples were heated to 200 °C at a heating rate of 10 °C/min.

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