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Seeding nuclei for the phase-separation of cellulose acetate solution

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ABSTRACT

In this paper, we report that fast evaporation of volatile solvent from cellulose acetate (CA) solution layer containing a proper nonvolatile alcohol can lead to the formation of relatively uniform nanoporous CA membrane. We propose that in the phase-separation process, the molecules of the nonvolatile alcohol aggregate to constitute the polymer-lean nuclei (PLN). These PLN exist stably (but not evaporate), grow continuously, and develop finally into the pores on the membrane. Relevant evidences are provided to support the proposed mechanism. This work implies a possible approach to generate uniform nanopores on polymer membrane.

1. Introduction

In the field of separation, polymer membranes with uniform pore size always are highly valuable [1]. The preparation methods of this kind of membrane mainly include the breath figure (BF) method [2], the block copolymer self-assembly (BCS) method [3], and the track-etching (TE) method [4]. The BF method can conveniently generate uniform pores on polymer membrane by using the condensed water droplets as template; however, it mainly applies to the polystyrene related polymers and the pore size hardly can be smaller than 100 nm [2,5,6]. The BCS method can generate highly uniform nanopores on polymer membrane and the pore size can be smaller than 10 nm; however, it is confined to the block copolymers, most of which are not the existing commercial products [3,7,8]. The TE method can generate uniform pores of broad size range (from micro to nanoscale) on polymer membrane; however, it applies to limited polymers such as polycarbonate and polyester [4,9]. Moreover, it involves expensive device and rigorous preparation conditions. In addition to the above methods, the phase-separation method also produces porous membrane. This method refers to inducing phase-separation to a cast polymer solution layer via immersing the layer into a coagulation bath, decreasing the temperature of the layer, or evaporating solvent from the layer [10,11]. The originally homogeneous polymer solution separates into the polymer-lean phase (nuclei) and the polymer-rich phase, the former finally develops into the pores on the membrane [10,11]. Though the method is simple, convenient, and applicable to many polymers, the formed pores are quite nonuniform [12], which largely limits the application of the membrane [12–14]. In this work, we found that the phase-separation method can generate relatively uniform nanopores on cellulose acetate (CA) membrane with the help of our seeded polymer-lean nuclei.

2. Materials and methods

2.1. Materials

Cellulose acetate (CA-398-30, M_n=50 K, Eastman) was used as the membrane material. Acetone (≥ 99.5%) and dioxane (≥ 99.5%) purchased from Sinopharm Chemical Reagent Co., Ltd. were used as the solvents of CA. Diglycol (≥ 99.0%), polyethylene glycol-200 (PEG200, chemically pure), PEG400 (chemically pure) and methanol (≥ 99.5%) purchased from Sinopharm Chemical Reagent Co., Ltd. were used as the nucleus agents. CA powder was dried in the oven at 104 °C for 2 h before use. All the other materials were used as received.

2.2. Membrane preparation

Different amounts of CA, solvent, and nucleus agent were weighed and added into a flask. The flask was sealed and the mixture was vigorously stirred (by a magnetic stirrer) at 40 °C for 6 h to obtain a homogeneous CA solution (refer to the figure captions

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for specific compositions). The CA solution was spin-cast on a silicon wafer (Speed I 1200 r/min for 3 s+Speed II 5000 r/min for 30 s, ambient temperature 20–22 °C, relative humidity 50–60%). After the casting, the formed membrane together with the wafer was immersed into the distilled water (21 °C) for 10 min to remove the residual solvent and nucleus agent, both of which are water-soluble. Then the membrane was peeled off from the wafer, covered on a porous support (a commercial polyvinylidene fluoride microfiltration membrane with nominal pore size of 0.22 μm, Shanghai Xinya Purify Device Company), and dried in the air.

2.3. Scanning electron microscope (SEM) observation

The dry membrane samples were fixed on a copper support (for the cross-section morphology observation, the samples were firstly fractured in liquid nitrogen and then were vertically attached to the sample stage) and sputtered with a thin layer of gold under vacuum. After that, the membrane morphologies were examined using a scanning electron microscope (Hitachi S-4800).

2.4. Determination of pore size distribution

The pore size distribution of each CA membrane was determined using the software "ImageJ". The procedure is shown below.

(1) Open the SEM image of membrane surface with "ImageJ"; (2) convert the image to a binary image by threshold segmentation; (3) separate the overlapping pores in the binary image by watershed segmentation; (4) set length scale for the binary image; (5) analyze the pore size (the range of pore size should be set) to obtain the size information of each pore; (6) construct the pore size distribution diagram using the obtained pore size information.

2.5. Solvent evaporation speed measurement

Different mixtures of the CA solvent and the nonvolatile alcohol (refer to Fig. 4 for specific compositions) were vigorously stirred at room temperature (18 °C) for 5 min. For each mixture, put certain amount of it (refer to Fig. 4 for the initial weight) into an open culture dish (diameter∗depth: 60 mm∗12mm) placed on a balance (d=0.1 mg, TP-114, Denver Instrument) and record the displayed weight every 20 s for 5 min. In the whole process, the left, right, and upper doors of the balance (placed in the fume cupboard, room temperature 18 °C, relatively humidity 34%) were kept open, the ventilation was kept in an "off" state since the wind influences the weight measurement. The slopes (absolute values) of the fitted lines of the weight–time points shown in Fig. 4 were used to reflect the solvent evaporation speeds.

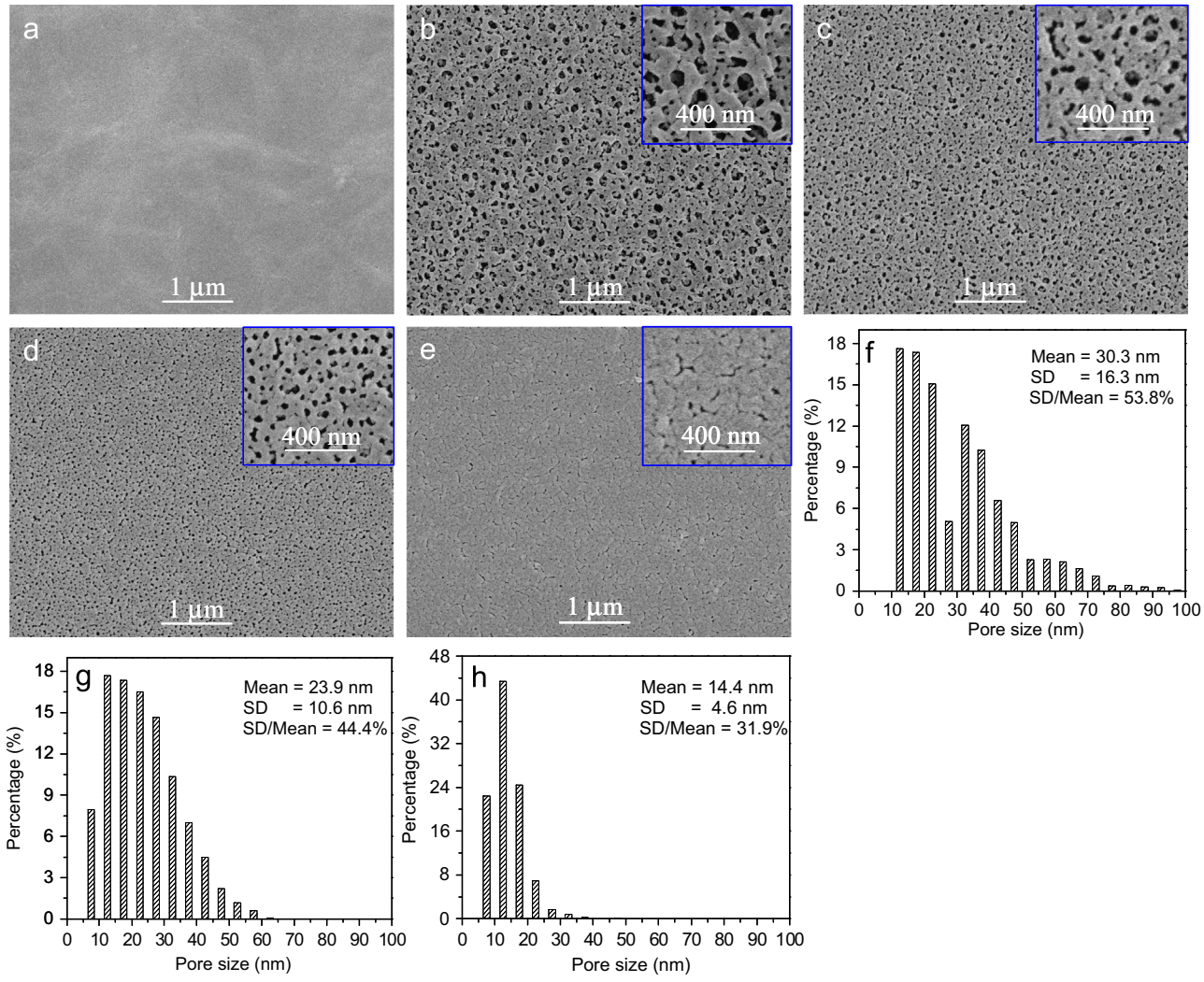

Fig. 1. Effects of CA content and PEG200 addition on the membrane structure. CA/(CA+acetone): (a) 2 wt%, (b) 2 wt%, (c) 3 wt%, (d) 5 wt%, (e) 7 wt%. PEG200/(PEG200+acetone): (a) 0 wt%. (b)–(e) 2 wt%. (f), (g), and (h) pore size distributions of membrane (c), (d), and (e), respectively. Mean and SD refer to the average pore size and the standard deviation, respectively.