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Formation of honeycomb structure films from polysulfone in a highly humid atmosphere

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ABSTRACT

By the water droplet templating method, regular honeycomb pattern polysulfone (PSf) films were prepared in a humid atmosphere. The effects of some factors on characters of regular honeycomb PSf films have been studied, such as, polymer concentration, solvent, the way of vapor intake, the position of the sample in the chamber. The results showed that (1) the average pore sizes of films first ascended with increase in polymer concentration then decreased when further increasing the polymer concentration, thus a maximum average pore size of 11.966 µm was observed at the polymer concentration of 45 g/l; (2) The vertical intake and the central location of the chamber were easy to form stable gaseous environment on the polymer solution surface, which induced to form the ordered honeycomb-structured film; (3) Comparing to CH_2Cl_2 and THF, $CHCl_3$ was the best solvent. However, the mixed solvent ($CHCl_3$/CH_2Cl_2) formed better honeycomb structure than single solvent, and the average pore size increased as the CH_2Cl_2 ratio increased.

Keywords: Honeycomb pattern; Water droplet templating method; Polysulfone; Polymer concentration; Solvent; High-humidity environment

1. Introduction

Recently, ordered porous films has attracted considerable attentions because of their great interests in many areas, such as, tissue engineering [1–3], controlled drug release [4], biology [5], chemically heterogenous patterned surface fabrication [6,7], opto-electronic devices [8], chemical sensors [9], scaffolds for catalysis [10], and so on. The formation of the regular honeycomb porous films by the water droplet templating method is one of the great development in the field of molecular self-assemble.

PSf is noted for its ability to resist deformation under load in a broad range of temperature and environmental conditions. It can be effectively sanitized with standard sterilization techniques and cleaning agents, remaining tough and durable in water, steam and chemically harsh environments. This stability makes PSf ideal for applications in the medical, pharmaceutical, food processing industries and water/wastewater treatment industries. Regular honeycomb film of PSf with micron-sized cells both on the film surface and inside the film have been successfully obtained by casting the polymer solution in high humidity environment. Pores in different size could be obtained by changing the humidity, the concentration of the solution, solvents, and so on [11,12]. Bormashenko [13] insisted that molecular weight exerted a decisive influence on the patterns makeup. Pore size and depth, distance between pores and specific porosity depended strongly on the polymer's molecular weight. Xu [14] prepared regular PSf honeycomb films with three kinds of PSf in different molecular weight (44,000, 56,000, and 75,000). The pore sizes of films with regular patterns were

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found to increase with increased humidity or molecular weight of PSf, and the pore size reduced as the polymer concentration increases. Sulfonated polysulfones (SPSF) with different sulfonation degrees was synthesized and then fabricated the honeycomb ordered porous film with $CHCl_3$ as solvent by the water droplet templating method. The introduction of the sulfonate groups to PSf was helpful to form highly regular patterns [15]. Tian [16] found that a good compatibility between the polymers and their solvents was beneficial for the formation of regular structures.

To study the formation mechanism of the ordered honeycomb-structure film of the hydrophobic polymer PSf, the effect of the concentration of PSf, solvent, the way of vapor intake (horizontal and vertical), the position of the sample on patterning were investigated in details by microscopic observation system and scanning electron microscopy (SEM).

2. Experimental

2.1. Material

PSf (η=0.52~0.65) was supplied by Shanghai Megavision Membrane Tech & Eng. Co., LTD. Chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2) and tetrahydrofuran (THF) (Beijing Chemical Corporation) chosen as solvents were spectroscopy grade. Water was purified by a reverse osmosis system (the electrical conductivity of the permeate < 5 μs/cm).

2.2. Film preparation and characterization

The high humidity induced process is an advancing method for preparing honeycomb porous films. Firstly, PSf was dissolved in solvent and then stirred by SHZ-82 constant temperature shaker (Guohua Instrument Factory, Jiangsu, China) for 24 h to obtain homogenous polymer solution. PSf solution was subsequently cast on a substrate and placed in a chamber with controlled relative humidity at ambient temperature. Water vapor was fed into the chamber few minutes. Then water droplets which condensed onto the surface of the polymer solution from damp air acted as the template. Basing on it the film with regular honeycomb pores was formed. Experimental flow chart was shown in Fig. 1.

2.3. The morphologies of the film

The surface morphologies of these films were characterized using the microscopic observation system and SEM (S-4300, Hitachi, Japan). The microscopic observation system contained a phase contrast microscopy, a computer and a charge-coupled device (CCD) system.

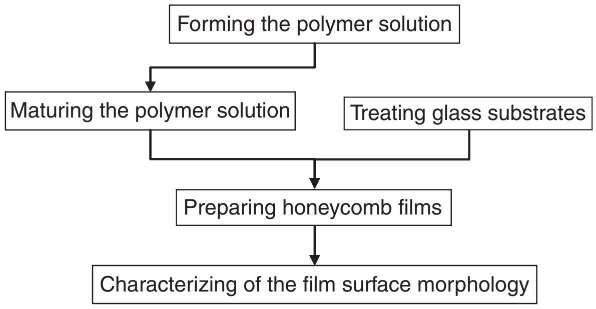

Fig. 1. Flow chart of honeycomb films prepared by water droplet templating method.

3. Results and discussions

3.1. Influence of polymer concentration

The concentration of polymer solution was closely related to the pore shape and size. $CHCl_3$ was chosen as the solvent to study the influence of the concentration of PSf on patterning. In the chamber, the relative humidity was maintained at 100% with ambient temperature.

Fig. 2 showed that the average pore size of the film ascended first and decreased later with PSf concentration increase. The shape of pores of the films was uniform,

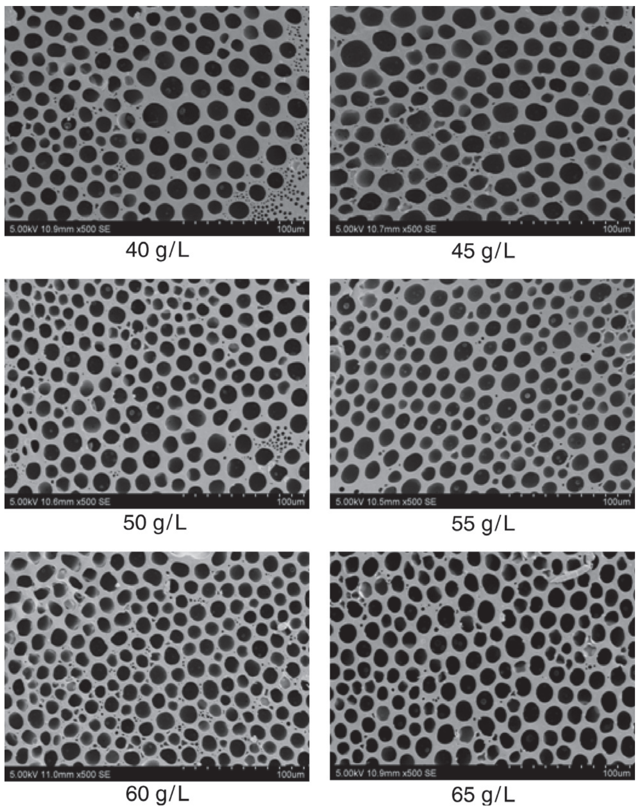

Fig. 2. SEM images of films for different PSf concentrations. Temperature: ambient temperature; relative humidity: 100%; solvent: $CHCl_3$.

but the size was different. The average pore size of the film was the biggest as the concentration of PSf was 45 g/l.

In general conditions, it is believed that polymer tends to form an extreme thin surface film on the surface of the solution to both reduce the surface tension of the emulsion and stabilize the water droplets in the solution to ensure the uniformity of the water droplets. PSf concentration influences the surface tension of the PSf solution. When the concentration of PSf increased from 40 g/l to 45 g/l, the average pore sizes of the films increased from 11.802 to 11.966 μm (Table 1); When the concentration of PSf was higher than 45 g/l, the greater the surface tension, condensation of water droplets immersed into the solution was more difficult, the formation of pore structure was more difficult, the average pore size of the film decreased from 11.966 to 10.108 μm with increase PSf concentration (Table 1). Comparing these images, the suitable polymer concentration was 50 g/l.

3.2. Influence of vapor intake

The effect of the ways of vapor intake on the film patterning was studied, which contained horizontal intake and vertical intake (Fig. 3). $CHCl_3$ was used as the solvent, and the polymer concentration was 50g/l. Same conditions in the chamber were maintained as mentioned previously.

The flow velocity of water vapor of horizontal intake on the polymer solution surface was much higher than that of vertical intake. Therefore, the environment on the polymer solution surface was dynamic and unstable. It was found in Fig. 4 that the average pore size and pore distribution in vertical intake were better than that in horizontal intake. That is to say, vertical intake was necessary to form the regular honeycomb film.

3.3 Influence of position of the sample

The experimental chamber consists of two layers, the distance between the upper and the roof of the chamber was 30 cm, and the distance between the lower and the roof of the chamber was 38 cm (Fig. 3). According to the experimental method, the glass substrate was placed on the upper and the lower respectively. The water vapor was poured in vertical intake, $CHCl_3$ was used as the solvent, the environment temperature was ambient temperature, the relative humidity was 100%, and the polymer concentration was 50 g/l.

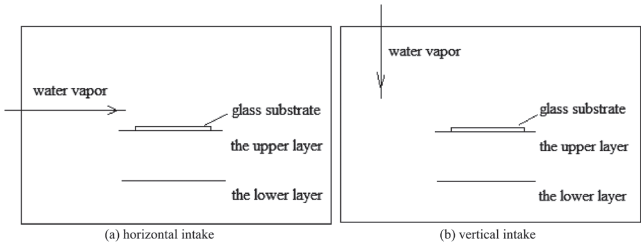

Fig. 3. The schematic diagram for the way of water vapor intakes.

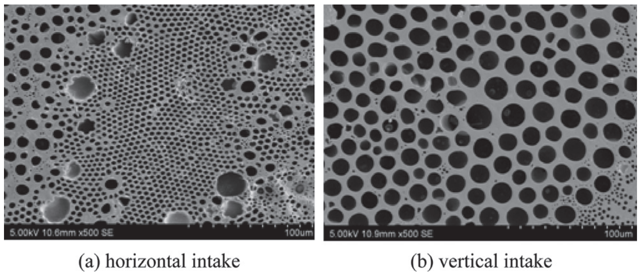

Fig. 4. SEM images of films for the way of vapor intakes. Temperature: ambient temperature; relative humidity: 100%; polymer concentration: 50 g/l.

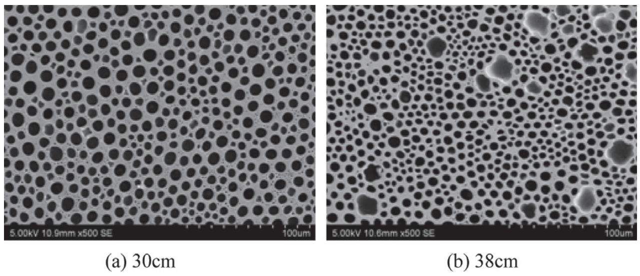

Fig. 5. SEM images of films for the different location of the chamber. Temperature: ambient temperature; relative humidity: 100%; polymer concentration: 50 g/l.

It was shown in Fig. 5 that the structure of the film was much better for 30 cm than for 38 cm. The reason was that the upper layer was in central location of the chamber, so the gaseous environment was much more stable.

Table 1
Average pore sizes of films for different PSf concentration. Temperature: ambient temperature; relative humidity: 100%; solvent: $CHCl_3$

Concentration of PSf (g/l)	40	45	50	55	60	65
Average pore size (μm)	11.802	11.966	11.620	10.324	10.145	10.108

3.4. Influence of solvent

CH_2Cl_2, $CHCl_3$ and THF were chosen to study the influence of solvent on patterning. In the chamber, the water vapor was poured in vertical intake, the sample of polymer solution was in the central position of the chamber, and relative humidity was 100% with the ambient temperature.

With the polymer concentration at 50 g/l, it was showed in Fig. 6 that more regular honeycomb pattern can be obtained when $CHCl_3$ was used as solvent compared to THF and CH_2Cl_2. And the pore size of the $CHCl_3$ was much larger than that of THF and CH_2Cl_2. The reason to this phenomenon was that solubility sequence of solvents in water was THF >> CH_2Cl_2 > $CHCl_3$, water droplets condensed from the air to THF surface then dissolved in THF, it did not form a honeycomb-like porous template but as non-solvent (additive) lead to the phase separation of polymer solution. Using $CHCl_3$ as solvent, water slightly dissolved in $CHCl_3$, polymer cut off coalescence between water droplets. Thus, water droplets would be arranged in honeycomb, making the formation of honeycomb porous template. Therefore, the porous honeycomb film was successfully prepared.

The volatility and the solubility of solvent in water are important factors for preparing ordered honeycomb-structured films. Thus, two solvents were mixed at an appropriate ratio to form a mixed solvent, which could combine the advantages of the two solvents. Therefore, blend solvents ($CHCl_3$ and CH_2Cl_2) were used to dissolve the polymers and form porous films.

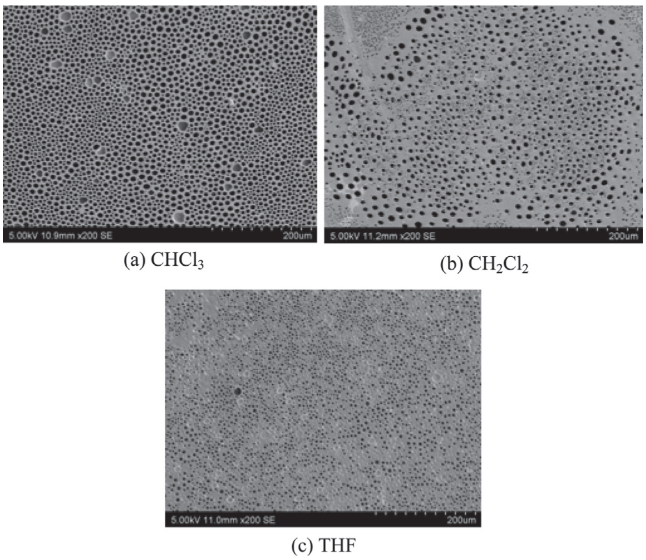

Fig. 6. SEM images of films for different solvents. Temperature: ambient temperature; relative humidity: 100%; polymer concentration: 50 g/l.

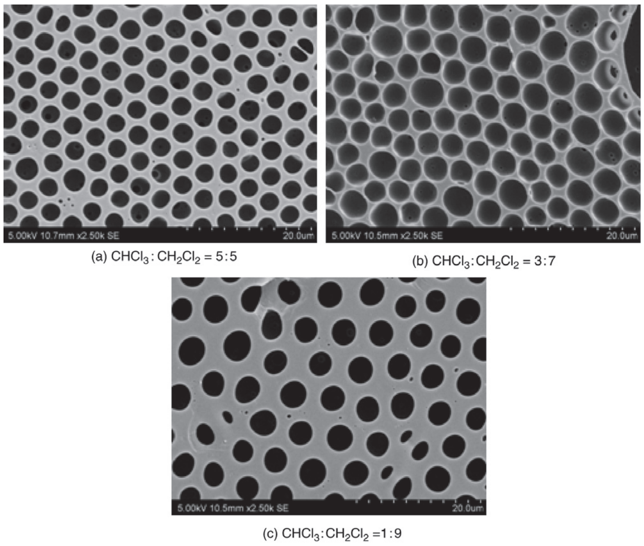

Fig. 7. SEM images of films for blend solvents. Temperature: ambient temperature; relative humidity: 100%; polymer concentration: 50 g/l.

As shown in Fig. 6 and Fig. 7, the mixed solvent ($CHCl_3/CH_2Cl_2$) formed better honeycomb structure than single solvent, and the average pore size increased as the CH_2Cl_2 ratio increased. This observation can be attributed to CH_2Cl_2 change the evaporation velocity of the blend solvent. The appropriate volatilization rate of the solvent was a key factor to fabricate honeycomb structure. The boiling point of CH_2Cl_2 was 39.8°C while that of $CHCl_3$ was 61.2°C, which meant CH_2Cl_2 led to a fast evaporation and consequently, a larger the temperature difference between the temperature of atmosphere and the temperature of the surface of polymer solution. Considering the nucleation time was short enough to be regarded as the same for all solutions, solution with a larger proportion of CH_2Cl_2 should form larger pores (Table 2). However, a larger proportion of CH_2Cl_2 meant that water droplets dissolved more easily in the blend solvent. In conclusion, it was safe to say that the best solvent mixing ratio was 5:5 ($CHCl_3/CH_2Cl_2$).

Table 2
Average pore sizes of films for blend solvents. Temperature: ambient temperature; relative humidity: 100%; polymer concentration: 50 g/l

$CHCl_3/CH_2Cl_2$ (V/V)	5:5	3:7	1:9
Average pore size(μm)	3.233	3.564	3.903

4. Conclusions

The PSf film with regular honeycomb pattern was prepared successfully. The average pore size of the film ascended first and decreased later with PSf concentration increase. The vertical intake and the central location of the chamber were easy to form stable gaseous environment on the polymer solution surface, which induced to form the ordered honeycomb-structured film. Comparing to CH_2Cl_2 and THF, $CHCl_3$ was the best solvent. However, the mixed solvent ($CHCl_3/CH_2Cl_2$) formed better honeycomb structure than single solvent, and the average pore size increased as the CH_2Cl_2 ratio increased. The ordered honeycomb structured film was successfully prepared with the following conditions: 50 g/l polymer concentration, $CHCl_3/CH_2Cl_2$ (5/5) blend solvent, the water vapor poured in vertical intake, the sample of polymer solution being in the central position of the chamber, 100% of the relative humidity in ambient temperature.

Acknowledgements

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