Porous Honeycomb Films Prepared from Poly (phthalazionone ether sulfone ketone) (PPESK) by Self-Organization Method

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ABSTRACT: Preparation of honeycomb-patterned films from Poly (phthalazionone ether sulfone ketone) (PPESK), one of the thermally stable polymers, in a humid atmosphere was reported in this article. The mechanism of forming honeycomb structure was discussed. Some influences, such as the effect of PPESK concentration and the atmosphere humidity were tested. Furthermore, the thermal stability of honeycomb-patterned films was also investigated, and it was shown that the honeycomb structures could be stable existed at 300°C. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 1524–1528, 2008

Key words: honeycomb; thermostability; PPESK; humid atmosphere

INTRODUCTION

Microporous films with honeycomb structures have attracted great interest due to their potential applications in chemical sensors,[1] photonics,[2] biotechnology,[3] and micrographics[4] etc. It was first reported by Francois and coworkers[5] using water microspheres as templates to fabricate ordered porous structures under high humidity. Hexagonally packed water droplets are formed by evaporation cooling on the solution surface and then transferred to the solution front in the convectional flow or by the capillary force. After the solvent and water droplets evaporated completely, the honeycomb-patterned polymer film is formed. For the convenience of manipulation, this method aroused much attention. Various types of polymer materials have been used to prepare honeycomb-like films, such as rod-coil block copolymers,[6] star polymers,[7,8] dendritic copolymers,[9,10] amphiphilic copolymers,[11–13] hydrophobic polymers[14,15] etc.

The polymers with thermal stabilities were widely employed in many fields due to their desirable characteristics such as resistance to heat, high mechanical properties, etc.[16,17] However, these kinds of polymer generally have a poor solubility in most solvents, which posed the limitation on their extensive applications. Erdogan et al.[18] and Yabu et al.[19] had prepared thermally stable honeycomb-patterned films by crosslinking of azide group or imidization of polyamic acids in highly humid atmosphere. However, it was also found these treatments destroyed the previous structures of the films in some degrees. Therefore, if using one kind of soluble thermopolymers to fabricate regular porous films in humid atmosphere directly, the following-up treatments could be avoided and the initial patterns could be remained. We have used some kinds of soluble thermopolymers to form honeycomb film, including semifluorinated polyimides[20,21] and polyetherketone cardo (PEK-C).[22] Here we used another excellent thermally stable polymer, poly (phthalazine ether sulfone ketone) (PPESK) to fabricate honeycomb-patterned films. This work raised the possibility that such structures could be formed by thermally stable polymer and extended the family of source materials.

PPESK is one of the most important high thermal performance engineering plastics that have been used in electronic, aircraft and aerospace industries, and membranes.[23–25] The chemical structure of PPESK is shown in Figure 1. PPESK has an aromatic heterocyclic twisted noncoplanar structure, which leads to perfect performance of well solubility, superior mechanical strength and chemical resistance and very high glass transition temperature (T_g) in the range of 263–305°C. These properties are very important to the performance and the life of the films.

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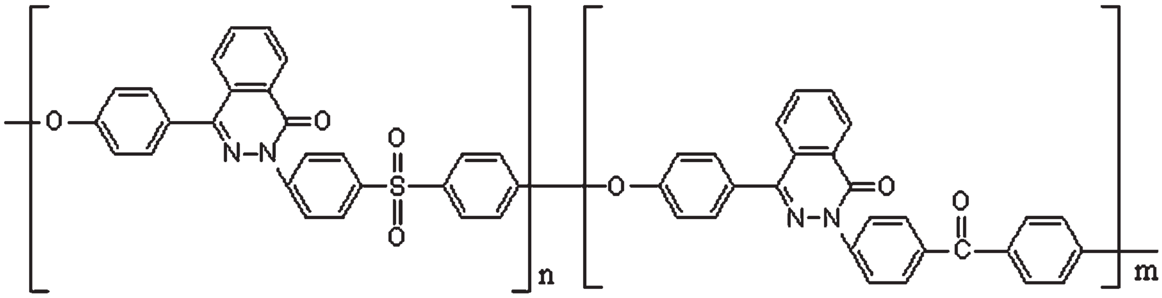

Figure 1 Chemical structure of PPESK.

In this article, the fabrication of honeycomb structure of PPESK in a highly moist environment was researched. Some affecting factors, such as the atmosphere humidity and the concentrations of the polymer solutions were tested. Moreover, the thermal stability of honeycomb-patterned films was also discussed.

EXPERIMENTAL

Materials

PPESK in powder form was obtained from Dalian Polymer New Materials (PR China). The weight-average molecular weight (M_n) of the PPESK was about 218,000. PPESK used in this research has a sulfone/ketone molar ratio of 1 : 1. It was dried at 100°C in vacuum for 12 h before use. Chloroform ($CHCl_3$) was purchased from Beijing Chemical Reagent, analysis grade. Water was purified by a Millipore system (Milli-Q, Millipore).

Film preparation

PPESK was dissolved in $CHCl_3$ and formed the PPESK/$CHCl_3$ solution with a series of concentrations. And then, 100 μL of PPESK/$CHCl_3$ solution was cast on a glass substrate at room temperature in a chamber whose relative humidity could be controlled. The solvent started to evaporate and condensed water droplets were deposited on the solution surface due to evaporative cooling. The water droplets were packed regularly by lateral capillary forces among themselves. The transparent polymer solution became turbid along with the solvent evaporation due to emulsification. After complete evaporation of the solvent and water, a thin opaque film with porous honeycomb-like structure was remained.

Measurements

Thermogravimetric analyses (TGA) was performed on a TGA-2050 thermal analyzer using a heating rate of 20 mL/min in N_2. The glass transition temperature was determined by differential scanning calorimetry (Seiko DSC200) from 100 to 400°C at the heat rate of 10 K/min.

The thermal stability of honeycomb-patterned films was investigated using a method of raising the temperature from room temperature to 350°C in a muffle (Wuhan Gongli Manufacturing, SX2-4-10, PR China) with a heating rate of 10°C/min. The surface morphology of the microstructured films was characterized by scanning electron microscopy (SEM), carried out on JEOL SEM4500 at 30 kV accelerating voltage and 10 μA.

RESULTS AND DISCUSSION

Mechanism of honeycomb on pattern formation

The process of forming the honeycomb films is used to be described as follows: (1) Water droplets are condensed at the surface of the solution due to the cooling by the solvent evaporation. (2) Because of the incompatibility of the organic solvent and water, as well as the hydrophilic/hydrophobic balance of polymer solution, water droplets are closely packed at the surface of the solution by lateral capillary forces among themselves. (3) After the water and the solvent evaporate completely, honeycomb films are prepared.

The capillary attractive force was an important factor during the formation of the honeycomb structure.[26] Peng et al.[27] deduced that at the first stage of the solvent evaporation, water droplets condensed on the surface of the solution and formed many isolated ''islands'' with ordered structures. These ''islands'' were then compactly arranged due to the Marangoni convection.[28] Xu et al.[29] considered that when the solution surface area decreased, these ''islands'' were pulled together, and collisions occurred. These collisions led to irregular border between ''islands.'' We believed that the neighbor-isolated water droplets were arranged and collided along with Marangoni convection simultaneously.[15,21] Whether or not the pores were regular depended on the competition of the arrangement and collision among the neighbor droplets, if regular arrangement was the main progress an ordered pat-

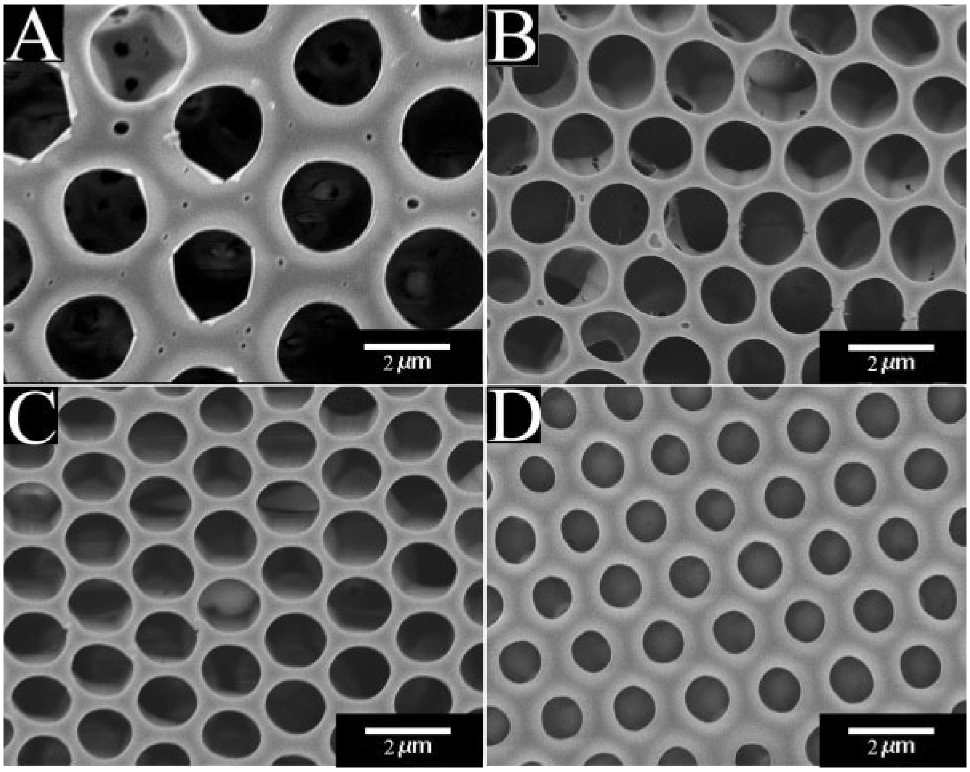

Figure 2 SEM images of the porous structure in PPESK films prepared from different solution concentrations. (a) 5, (b) 10, (c) 20, and (d) 50 g L^{-1}. Other conditions: temperature 30°C, relative humidity 95%, spreading volume 100 mL.

tern would be formed. Manly factors would influence this progress, such as the solution concentration, the humidity and the solvent evaporation rate, etc.

Influence of concentration

After casting 100 μL PPESK/$CHCl_3$ solution on a glass slide, the solvent began to evaporate and some phenomena were observed immediately. It could be easy to see that, with the volatilization of the solvent, the transparent polymer solution became turbid due to emulsification. When the solvent volatilized completely, an opaque and cream-colored layer left. The thicknesses of the films are about 6–9 μm according the different of the solution concentration.

A series of polymer solution concentrations, ranged from 0.5 to 50 g L^{-1}, were prepared to investigate the influence of polymer solution concentration. It was found the PPESK/$CHCl_3$ solution with lower concentration could not form regular pattern, and only at high concentration (>5 g L^{-1}) regular patterns could be achieved. Figure 2 shows the SEM images fabricated from various PPESK/$CHCl_3$ solution concentrations (5, 10, 20, and 50 g L^{-1}). It can be seen in Figure 2, the pore size decreases from about 2–0.9 μm as the concentration increasing, and the pores become more regular.

We believed this phenomenon was caused by the congregation of PPESK on solution surface. It was reported by us[21,23] that the congregated molecules

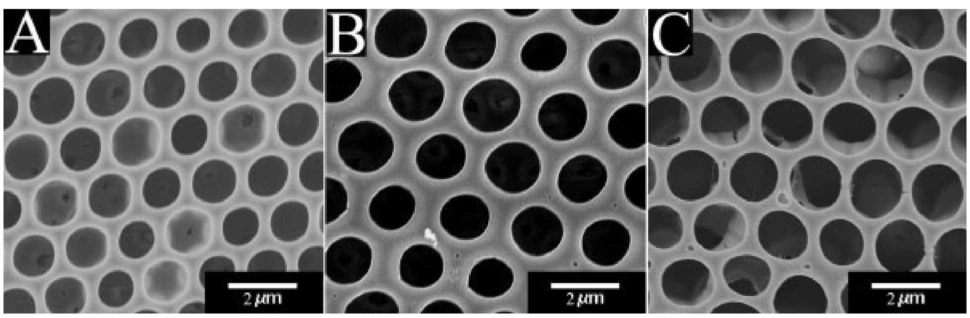

Figure 3 SEM images of the porous structure in PPESK films prepared from various humidity. (a) 80, (b) 85, and (c) 95%. Other conditions: temperature 30°C, concentration 10 g L^{-1}, spreading volume 100 mL.

TABLE I
Thermal Properties of PPESK

Polymer	T_g (°C)	T_d (°C)
PPESK	283	501

would form a thin liquid film on the solution surface. This thin liquid film was important on pattern formation because it could stabilize the cooled water droplets. The solution concentration could influence the strength of thin surface film, easily. When the concentration of the polymer solution was low, little PPESK molecules could gather at the interface between the solution and air, the strength of this liquid film was weak and neighboring water droplets could easily coalesce, resulted in irregular pattern. When the polymer solution concentration increased, the polymer solution contained more PPESK molecules to enforce the strength of the liquid film, which finally was strong enough to stabilize water droplets. Stably existed water droplets were the key factor to form honeycomb films, because water droplets were a template for the porous structure. Only regular arrangement of microspheres led to regular patterns.

Influence of humidity

Humidity of atmosphere is another important factor on pattern formation. To investigate the influence of the relative humidity on pattern formation, 10 g L^{-1} PPESK/$CHCl_3$ solution was used to fabricate porous polymer films. The humidity had been set to 80, 85, and 95% respectively, while keeping other conditions constant. As shown in Figure 3, the pore size enlarged from about 1.0–2.0 μm with an increase of humidity. Moreover, the pores were more regular as the humidity increasing.

The two-dimensional array of water microspheres was a template for the porous structure of the honeycomb film, and the size of a water microsphere was one of the determining parameters of the pore size. The humidity of the atmosphere influenced the water condensation at the air-polymer solution interface and, consequently, influenced the pore size and regularity of the micropore arrangement. It was safe to say that high humidity was needed to form orderly porous films for this polymer. The regularity of the water droplets arrangement at high humidity was best compared with those at others.

Evaporation at low humidity (<80%) gave nearly no regular pores on the polymer film, owing to no enough vapor in atmosphere condensing onto the solution surface. In this situation, increasing the evaporation rate of the solvent can obtain regular patterns in a low humidity,[21] which led to an enough temperature gradient that caused the condensation of water vapor.

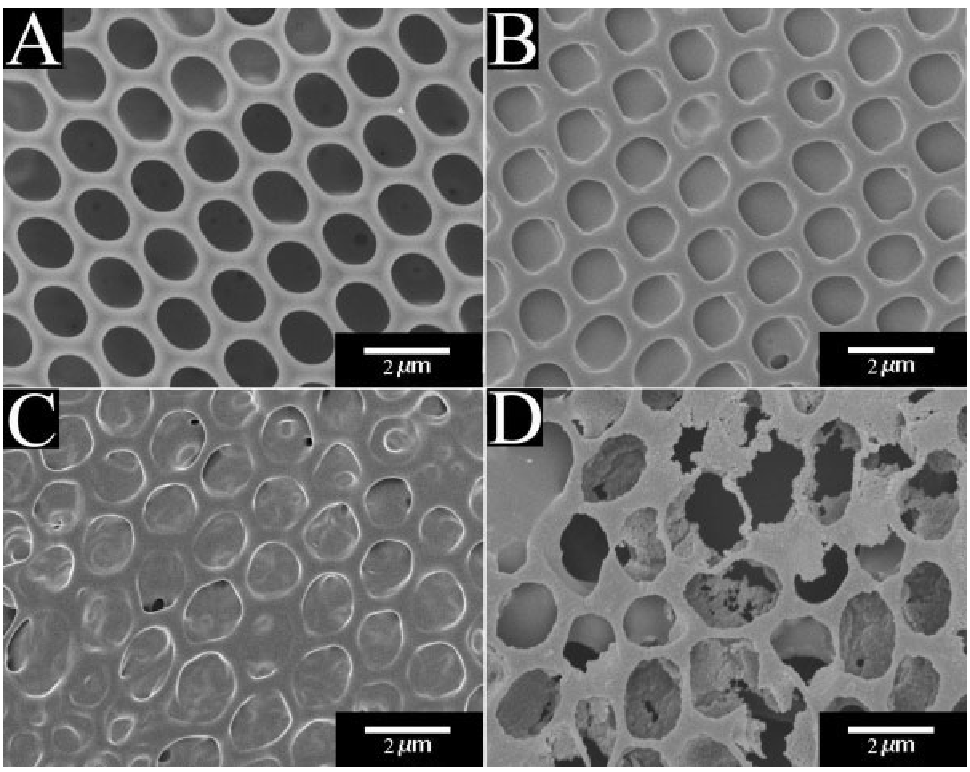

Figure 4 SEM images of the porous structure in PPESK films heated at different temperature. (a) 200, (b) 260, (c) 300, and (d) 350°C. Other conditions: concentration 20 g L^{-1}, spreading volume 100 mL.

The thermal stability of honeycomb-patterned films

Thermal properties of PPESK were characterized using DSC for testing the glass transition temperature (T_g) and TGA for the decomposition temperature (T_d). Thermal behavior data of PPESK were summarized in Table I. A glass transition was observed at 283°C (T_g), demonstrating the admirable rigidity of PPESK. The TGA analyses showed 5 wt % loss of PPESK at 501°C (T_d), showing its good thermal stability.

To evaluate the thermal stability of the honeycomb films, four pieces of films, with the solution concentration of 20 g L^{-1} and fabricated under same conditions, were respectively, heated from room temperature to 200, 260, 300, and 350°C in a muffle, and then kept the temperature for 1 h. Figure 4 shows the SEM results of these heated films. As can be seen, the film heated to 200°C is nearly no change comparing with those of not heated. The film keeps its honeycomb structures by and large at 260°C, only a little deformation of the pores. The surface of the film has the clearly tendency to collapse to the bottom at 300°C, and when the temperature reaches 350°C, the polymer film deforms drastically. The pattern is destroyed and honeycomb structure disappears. This can be easily understood that with the increasing of temperature, the mechanics state of the polymer changes from glassy state to elastomeric state gradually, which leads to the easy deformation of the polymer, especially the temperature surpassed 283°C, namely T_g.

This result testified that the honeycomb films prepared from PPESK maintained its regular structures at high temperature, which showed the good thermal durability of PPESK films.

CONCLUSIONS

Honeycomb-patterned films were fabricated from PPESK, one of thermally stable polymers, in a humid atmosphere. A glass transition was observed at 283°C (T_g), demonstrating the admirable rigidity of PPESK. The TGA analyses showed 5 wt % loss of PPESK at 501°C (T_d), showing its good thermal stability. PPESK could only form honeycomb films at high concentrations, and as the concentration increasing, the pore size decreased from about 2.0–0.9 μm, and the pores became more regular. The pore size enlarged from about 1.0–1.6 μm with an increase of humidity at the concentration of 10 g L^{-1}. The humidity of the atmosphere influenced the water condensation at the air-polymer solution interface and, consequently, influenced the pore size and regularity of the micropore arrangement. The thermally stability of honeycomb-patterned films was also tested. It was shown that the honeycomb structures were stably existed less than 300°C.

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