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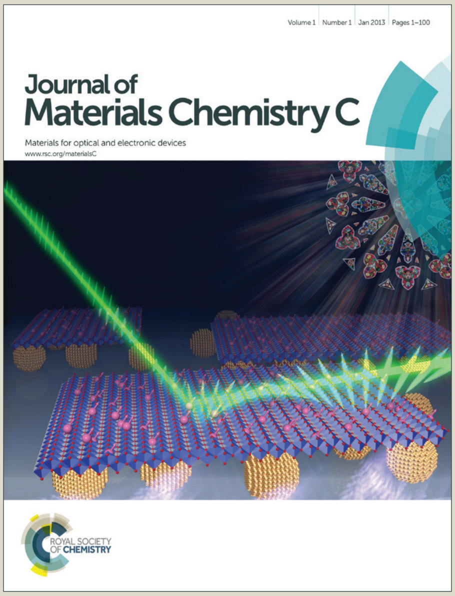

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Fabrication of porous film with controlled pore size and wettability by electric breath figure method

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Abstract

A novel electric breath figure, EBF, method was developed by applying an electrostatic generator to assist the common breath figure, BF, method, and applied to fabricate polystyrene, PS, film. FESEM images showed that these PS films have porous structure with controlled pore size because the average pore diameter, $\mathbf{d_a}$, of those PS films was about 2.30μm at 0V and gradually reduced to about 0.35μm at 1000V to follow a relationship as: $\mathbf{d_a}=a-b\ln(\boldsymbol{\rho}+c)$, where the $\boldsymbol{\rho}$ is the voltage and *a,b* and *c* are three constants. Wetting results showed that the water contact angle, $\boldsymbol{\theta_w}$, on these PS films was also controlled because the 0V PS film showed a $\boldsymbol{\theta_w}$ value at 95.07^0, and it was increased to at 147.09^0 when the $\boldsymbol{\rho}$ increased to 1000V correspondingly. The reason on this EBF can control formation of porous film was found due to the surface tension of water reduced with the voltage increase.

Keywords: Electric breath figure; porous film; polystyrene; pore size; wettability.

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Introduction

Thin porous films over a range of pore sizes have attracted great attentions due to their wide applications.[1-7] Porous films can be successfully fabricated by a lot of methods, e.g. the photolithography,[8] soft lithography,[9] and templating methods which including the breath figure, BF, method.[10-12] As known, the BF is a simple and economic method because it use water droplets as template[12] as compared with other templating methods.[10,11]

The BF method is usually performed in a humid condition by evaporation of organic solvent to reduce the surface temperature and make water droplets condense on the surface then subsequently grow.[11-13] After some times, the droplets would be self-assembled into a well-ordered hexagonal array by thermofluid dynamic movements when the polymer concentration increased with the solvent evaporation to lead the polymer precipitated on the interface to stabilize the droplets and prevent coagulation.[13] Once the solvent evaporation fully completely, high ordered porous structure would be appeared due to the water droplet array as a template.[11-13] The BF method can control the pore size of polymer films by varying the conditions, e.g. the humidity level, solution concentration, temperature, the size of water droplet, air speed, and polymer molecular weight.[14-21]

By applying an electrostatic generator to assist the common BF method to form an electric BF, EBF, method, in this paper we reported that this novel EBF method can form porous film with controlled pore size and wettability. Experimentally, the often used linear polystyrene, PS, was employed as an example, and all EBF fabricated PS films were compared with literature reported cases.

Experimental

Materials

Liner PS with known molecular weight, W_m=184,000, obtained from Qiancheng Co., Ltd, Zhengjiang, China, was used as received.

Carbon disulfide in analytic grade obtained from Sinopharm Chemical Reagent Co., Ltd, China was used as received.

Distilled water prepared in our lab was used through whole experiment.

Formation of high ordered porous PS films via electric breath figure method

The as-received PS was initially dissolved in CS_2 to form a polymer solution with a concentration at 1 wt%. The PS/CS_2 solution was then casted onto the glass substrate to allow the airflow across the surface where an electrostatic generator (ES203, Shanghai Lingshi Electrical Co., China) was applied to control the air flow as Fig. 1 described by taking two electrodes to link two copper plates to influence the polymer solution across the surface. During this EBF process, the total time for preparation of each sample was about 3 min. It is obviously that this is a novel electric BF process, EBF. In this work, the voltage was applied at 0, 100, 200, 600 and 1000V, respectively. Other condition parameters were fixed, e.g. the distance between two coppers fixed at about 1 cm, the related humidity of the airflow and the drop flow velocity fixed at about 75% and 50m/min, respectively, and the temperature was controlled at about 25℃.

Figure 1

Characterization

The pore structure and size of PS films was characterized by field emission scanning electron microscopy, FESEM, (JSM-5600LV; JEOL, Japan).

The water surface tension under extra electric voltage was measured by using a modified platinum plate surface tension measurement method by applying an electrostatic generator (ES203, Shanghai Lingshi Electrical Co., China) to link both the platinum plate and water. In this measurement, the applied voltages were varied from zero to 9 kV.

The wettability was studied by measuring the drop water contact angle on PS film surface by using a ramé-hart Model 590 goniometer. The advancing contact angle was employed and the values were estimated according to associated grayscale images software. Before this measurement, the film surface was peeled off using adhesive tape (Scotch Tape, 3M) as the same as literature.[22]

Results and discussion

Effect of applied voltages on the pore structure and size of PS films

FESEM images of five prepared PS films in relation to applied voltages at 0, 100, 200, 600 and 1000V were showed in Fig. 2, respectively. Observed that these PS films all showed porous structure and the pore size was gradually reduced with the applied voltage to increase. For example, in terms of the statistics of the average diameter, $\mathbf{d_a}$, it was found that the pore for electricity-free sample was at about 2.30μm, and it was reduced to about 0.35μm for EBF sample corresponding to the voltage, **ρ**, at 1000V. In order to understand the relationship between the $\mathbf{d_a}$ and **ρ,** a plot was made as also showed in Fig.

2 (right bottom). Noted the deduced relationship between these two parameters was appeared as: $\mathbf{d_a}=a-b\ln(\boldsymbol{\rho}+c)$, where a, b and c are three constants.

Figure 2

These results implied that this novel EBF method is not only capable for applying to fabricate porous structure with controlled pore size, but also in forming the small size. Though the pore structure of film was known influenced by a lot of factors,[13-25] this novel EBF method exactly provided a possibility for simple controlling the pore size by varying only the voltage. In other words, this method has more adjusting possibilities than the common BF method.

Table 1

Considering the fact that the porous PS film was broadly studied using BF method, to compare the pore size of our sample with literature reported samples is required and necessary. Therefore, Table 1 quantitatively summarized the pore size reported by using the BF method and this case using the EBF method. Since these values all related the linear PS, it is found that the pore size of our 0V-sample showed similar scale as that of Srinivasarao et al.,[20] Peng et al.,[21] Ferrari et al.[22] and Zheng et al.[23] (Table 1). This is reasonable and strongly supports our other values. In Table 1, the 1000V-based PS film showed the pore diameter at about 350 nm, which is obviously smallest than that of the BF method based values.[18-27] In fact, it is also found that this EBF method produced the smallest pore size of linear PS film (Figure 2, Table 1) is also comparable to the 18-arm PS star yielded pore size.[19]

Effect of applied voltages on the wettability of porous PS films

Wettability is an important parameter of materials including the porous film[19] because the pore size in different scales can fit various applications.[12] Porous films usually display a highly hydrophobic character because the hydrophobic polymer matrix combined with air entrapped inside the pores which lead the surface roughness increase.[15,19] Due to the presence of a polymer and air, these porous films can be considered as composite materials in which both phases contribute to the contact angle.[19]

Taking the water as probe to study the wettability of those formed PS films, the water contact angles were also appeared in Fig. 2. In terms of the presented plot, the voltage increase from zero to 1000V caused the water contact angle increase from about 135 to 148^0, respectively. The 0V sample presented wetting result is interested because it was enhanced about 42% than that of the common non-porous PS film, e.g. the θ_w at about 95^0. This suggests that the use of EBF method to form film can enhance the hydrophobicity. The hydrophobicity of EBF method prepared PS films has been also found greater than that of the PS-b-PAA film.[19]

Mechanism on the EBF formation of porous PS film

Figure 3

In order to understand the mechanism of this novel EBF method can form porous structure with controlled size, the surface tension of water influenced by applied voltages must be investigated because the key difference between the common BF and the EBF is in the latter using electricity as assistance. Taking the surface tension of water as a function of the applied voltages, Fig. 3 showed a plot indicated that the surface tension of water was reduced with the voltage increase. In this Fig.3, a critical surface tension of water was found at about 42mN/m corresponding to a critical voltage at about 5 kV due to the surface tension stabilized since this point once the temperature fixed at 25℃. This important explained the reason why EBF method can form smaller pore size than that of the normal BF method is due to the former utilizing lower surface tension solution.

On the basis of Fig.3, the mechanism on using EBF to form porous structure with controlled pore size is primarily understood and available explained and described by Fig.4. Because the surface tension of water droplet was reduced with the voltage increase as described in Fig. 3, this leads the contact angle between the water drop and PS solution changed correspondingly as Fig. 4 described to cause the water droplets showing both the positive and negative centers to provide two possibilities, i.e. the one under the extra electrostatic force condition formed smaller water droplets which integrated to form big drops to cause the force between *b-c* and *c-d* as a trend to coalesce small and individual water droplets as bigger one; and another one, however, on the contrary because the presence of the electrostatic force between the positive and negative electrodes provided a significant opposite effect on each water droplet to cause the force between the positive electrode-*a*, *a-b, d-e, e*-negative electrode to form a trend to separate *b* and *d* from *c*. The low surface tension of water would influence the formation of porous structure is in good agreement with literature.[19]

Figure 4

Conclusion

By applying an electrostatic generator to assist the common BF method to for a novel EBF process, this work has proven that the formed porous structure would have controlled pore size and enhanced the hydrophobic for formed porous PS film. For linear PS, experiment has found that the pore size could be formed at about 350 nm known smaller than currently literature reported values.

The use of the EBF method to form porous film has advantages in the use of less process parameters because of the variety voltage available.

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Legends of Tables and Figures

Table 1. Comparison of the average pore diameter of porous PS films prepared in this work using the electric breath figure, EBF, method in relation to the voltage at 0, 100, 200, 600 and 1000V, respectively, and reported by literature all using the similar linear PS. M_w-molecular weight, RH-related humidity, CD-carbon disulfide, X-unknown.

Figure 1. Scheme on fabrication of porous PS film *via* the electric breath figure method.

Figure 2. FESEM images of porous PS films prepared via the electric breath figure method in relation to applied voltages at 0, 100, 200, 600 and 1000V, respectively.

Figure 3. Effect of applied voltages on the surface tension of water.

Figure 4. Mechanism on formation of porous PS film *via* the electric breath figure method.

Table 1

d$_a$ (μm)	M$_w$ (kg/mol)	Solvents	Voltage (V)	RH (%)	Refs
0.35±0.32	184	CD (1wt%)	1000	75	This work
0.76±0.32	184	CD (1wt%)	600	75	This work
1.00±0.33	184	CD (1wt%)	200	75	This work
1.21±0.06	184	CD (1wt%)	100	75	This work
2.30±0.25	184	CD (1wt%)	0	75	This work
2.78±0.38	192	CD (X)	0	75	(22)
2.50±0.50	50	CD (0.1-5wt%)	0	X	(10,20)
1.40	X	CD (X)	0	60	(24)
10.00	X	Benzene (5wt%)	0	80	(25)
2.00	223.2	Toluene (1wt%)	0	50	(21)
3.00	208	Chloroform (1wt%)	0	85	(23)
13.50	X	Chloroform (5wt%)	0	80	(25)

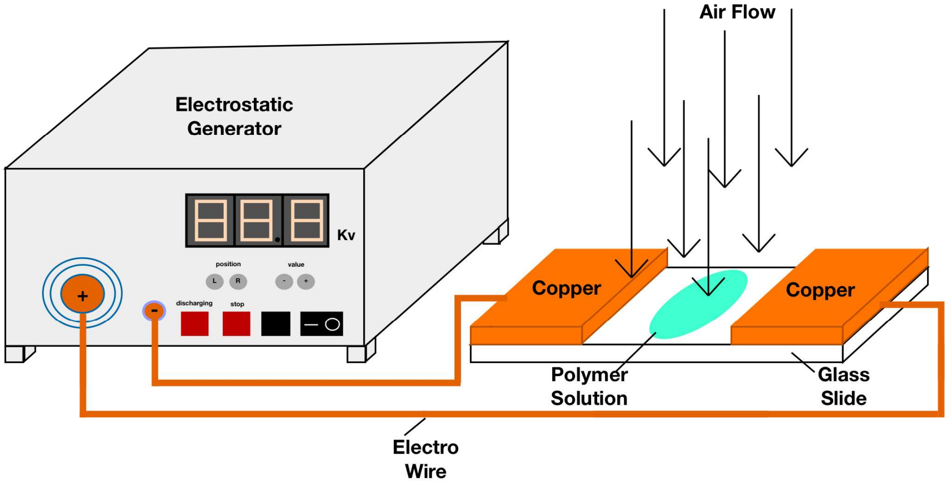
Air Flow
Electrostatic
Generator
Kv
position
value
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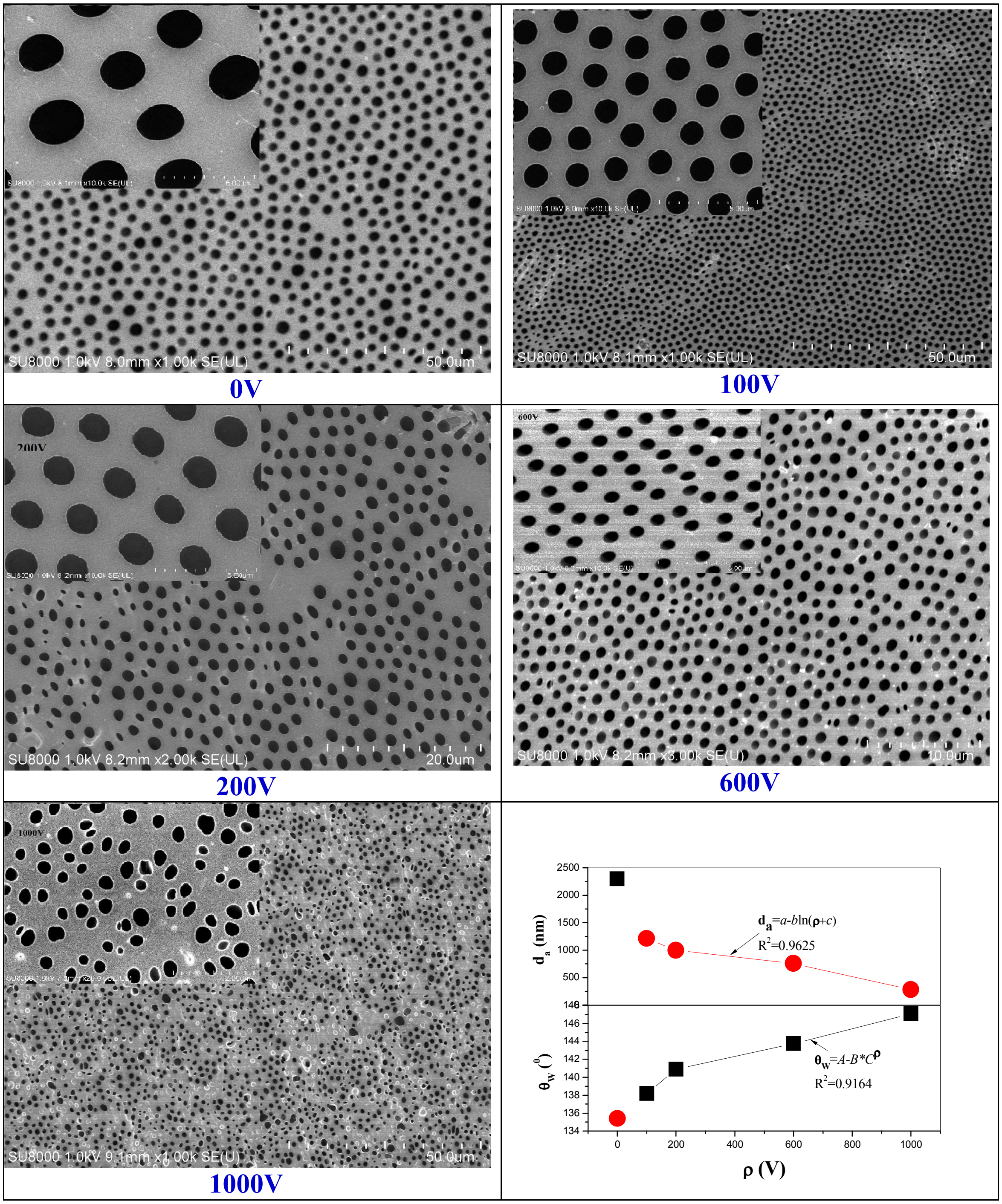
Figure 1



0V **100V** **200V** **600V** **1000V**

Figure 2

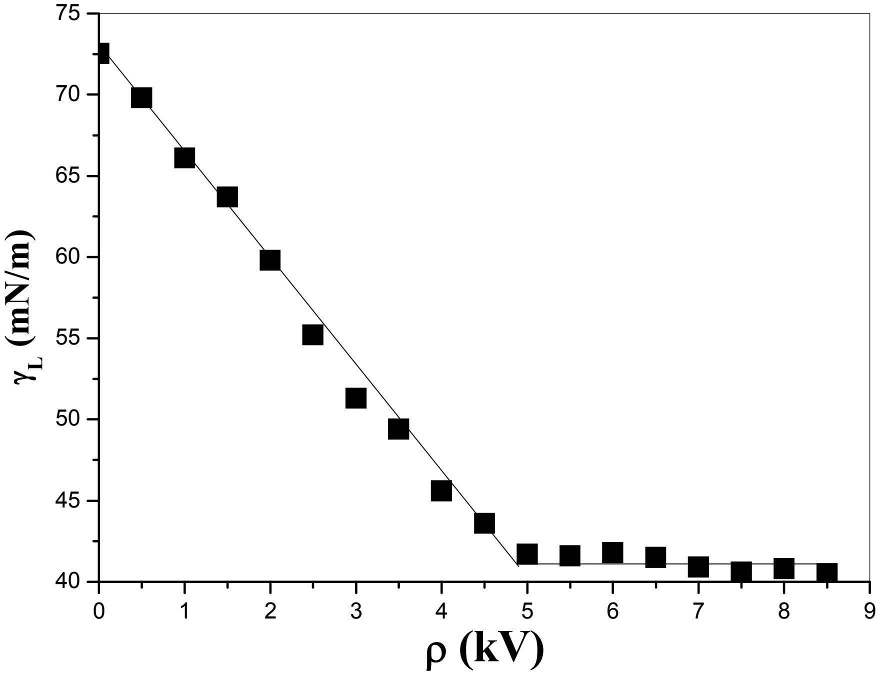


Figure 3

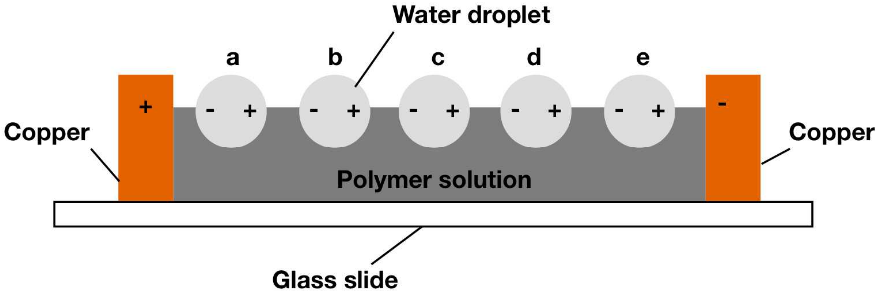
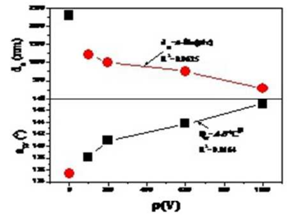


Figure 4

Graphical abstract



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