

Preparation and Properties of the Phenolic Foams with Controllable Nanometer Pore Structure

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ABSTRACT: Phenolic foam with nanometer pore structure and high strength was prepared by using a novel foaming method of phenol–formaldehyde novolac resin solution under pressure. Pore structure and the effects of pressure and resin concentration on it were investigated. Results showed that the mean pore size decreases from 800 to 30 nm with the increase of resin concentration from 0.08 to 0.36 g/mL. The pressure has a great effect on the pore structure and an optimal range (2.0–4.0 MPa)

at which the pore size is small in level of nanometer and has a good distribution. The nanometer pore structure resulted in significant improvement of compressive strength and thermal insulation properties of phenolic foam. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 3545–3550, 2010

Key words: phenolic resin; foam; microstructure; strength; nanometer pore

INTRODUCTION

Polymeric foam is widely studied and used recently and continues to grow at a rapid pace. Phenolic foam is important polymeric foam. Phenolic foam was first produced in the United States in 1937. The fine pore structure and chemical structure give phenolic foam excellent properties, including low flammability, high heat and solvent resistance, high dimensional stability and strength, low thermal conductivity and low toxicity.^{1,2} As a result, phenolic foam is particularly attractive for civil construction, passenger and military aircrafts, marines and electronic applications.

Preparation technique has an effect on the pore structure of phenolic foam. Phenolic foam is typically prepared by blending phenolic resin with foaming agent, surfactant, curing catalyst, and other additives homogeneously, followed by foaming. For the conventional phenolic foam, chlorofluorocarbons and other halogenated hydrocarbons and their derivatives were used as the foaming agents.^{3–5} However, the use of these blowing agents is limited recently due to environmental concerns. Recently, some efforts have been devoted to use pentane or other hydrocarbons as the foaming agent.^{6,7} However, the large pore size in micrometer scale and inhomogeneous distribution of the phenolic foam produced from

these aforementioned methods usually lead to poor mechanical strength and thermal insulation properties. Recently, searchers have developed some new foaming techniques (such as block copolymer,⁸ carbon dioxide,⁹ and polymer nanocomposites¹⁰ foaming methods) to obtain polymer foam with nanoporous structure. Polymer foam with nanoporous structure has some novel electrical, mechanical, and thermal properties.

In this study, we develop a novel foaming method of resin solution under pressure to fabricate phenolic foam (with nanometer pore structure) by using phenol–formaldehyde (PF) novolac resin as the raw material. It should be noted that the method uses anhydrous ethanol as solvent of phenolic resin and foaming agent in foaming stage without any other foaming agent, surfactant, or catalyst. The prepared foam has controllable nanometer pore structure and good thermal insulation properties and compressive strength.

EXPERIMENTAL

Materials

PF used in this study was prepared by the polymerization of phenol and formaldehyde (mole ratio 1 : 0.8) using oxalic acid as catalyst, then filtration and purification. The softening point, residual phenol content, and elemental content of the prepared resin were shown in Table I. The softening point and the residual phenol content of resin were measured according to the standards of ISO 3146-1985 and ISO

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TABLE I
Fundamental Properties of the Resulting Phenolic Resin

Free phenol content (wt %)	Softening point (K)	Elemental analysis (wt %)		
		H	C	O
≤3	403	7.3	76.2	16.5

8974-2002, respectively. Elemental content was measured by using a Vario EL atom analyzer. Hexamine (Tianda Chemical Factory, China) and anhydrous ethanol (Tianda Chemical Factory, China) were selected as curing agent and solvent, respectively.

Preparation of phenolic foam

PF, containing 9% hexamine by weight, was dissolved into anhydrous ethanol to form 0.08, 0.10, 0.18, 0.30, and 0.36 g/mL five solutions. Then these solutions were placed into an autoclave to heat and foam at 443 K at a heating rate of 0.2 K/min and then held there for 10 h under 3.0 MPa. When heated to 443 K, the pressure inside autoclave was released at a rate of 0.3 MPa/h. After being released, the samples were heated to 573 K and then held there for 4 h. The phenolic foams derived from the five solutions under 3.0 MPa were denoted as F08-3.0, F10-3.0, F18-3.0, F30-3.0, and F36-3.0, respectively. For studying the effect of the pressure on the pore structure of the foams, the solution (0.18 g/mL) was selected to foam under 1.5, 2.0, 2.5, 3.0, 4.0, and 5.0 MPa, respectively. The phenolic foams derived from this solution (0.18 g/mL) under different pressure were denoted as F18-1.5, F18-2.0, F18-2.5, F18-3.0, F18-4.0, and F18-5.0, respectively. In experimenting, the temperature was controlled by using a tempera-

ture control equipment (SKW-400, has an accuracy of ± 0.1 K and maximum temperature of 1573 K). The autoclave was pressurized to setting pressure in N_2 , which was controlled by a pressure regulator (YT-4). The size of the produced sample was about 100 mm \times 100 mm \times 30 mm.

Characterization

The microscope morphologies of the samples prepared were characterized on a JSM-6700 Field Emission Scanning Electron Microscope (SEM). Pore size distributions of these samples were measured on a Micromeritics Autopore IV 9500 mercury porosimeter. The mercury filling pressure applied to the sample was varied from about 0.70×10^{-3} to 207 MPa. The equilibration time was 30 s. The range of mean pore size measured was between about 360 and 0.005 μm . The intrusion accuracy of Autopore IV 9500 was $\pm 1\%$ of full scale intrusion volume. Adopting the standard of ASTM D1621-2000, the compression testing was carried out by Universal Testing Machine (INSTRON 8531) at a loading rate of 1 mm/min, and the compressive strength was calculated based on the "10% deformation" method according to the standard. The thermal conductivities of these samples were measured by using thermal constant analyzer (HOT DISK 2500S) at 293 K.

RESULTS AND DISCUSSION

Microscope morphology of the phenolic foam

Figure 1 shows the SEM images of a typical sample (F18-3.0, 0.27 g/cm³). From Figure 1, it can be seen that the sample has a gel-like three-dimensional framework with nanometer pore, in which the shape of

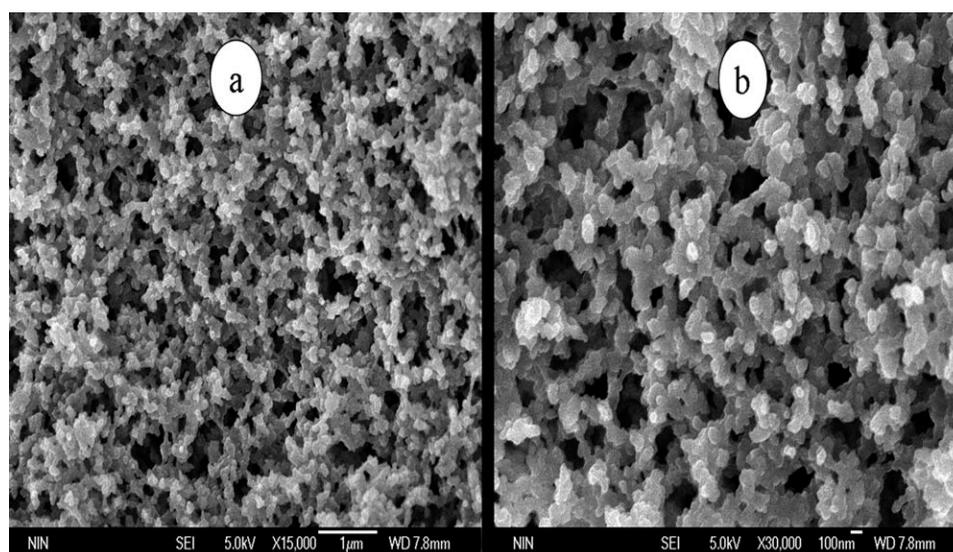


Figure 1 The SEM microphotographs of the phenolic foam (F18-3.0, 0.27 g/cm³): a, $\times 15,000$; b, $\times 30,000$.

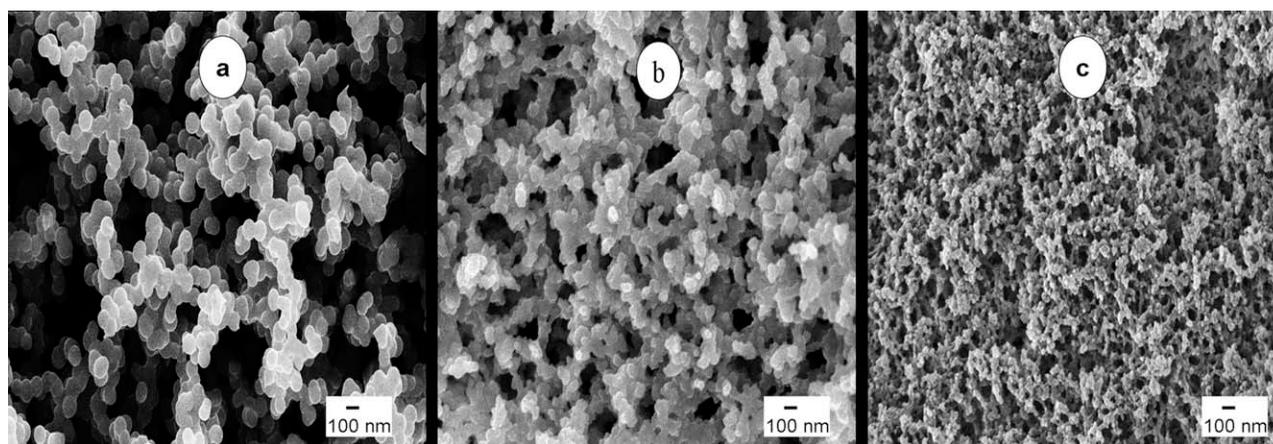


Figure 2 SEM microphotographs of these phenolic foams produced at 3.0 MPa pressures and different resin concentrations: a, 0.08 g/mL; b, 0.18 g/mL; c, 0.36 g/mL.

the phenolic nanoparticles is regular, and size is about 100 nm. There are many nanometer pores (150–250 nm) among the resin nanoparticles. Such good nanometer pore structure of phenolic foams shows a great contrast with that of phenolic foams (pore size is in the level of micrometer and inhomogeneous) derived from conventional methods.^{7,11,12} The comparison indicates that the pore size, and its distribution of phenolic foam are improved by using this technology. Two factors are responsible for the evolution of nanometer microstructure of phenolic foams; one is the dissolution of fine resin particle in anhydrous ethanol, and the other is the presence of pressure in autoclave in foaming stage.

Effect of the resin concentration on the pore structure

The resin concentration has a large effect on the pore structure of the produced foam. Figure 2 shows the SEM images of these foams produced at 3.0 MPa

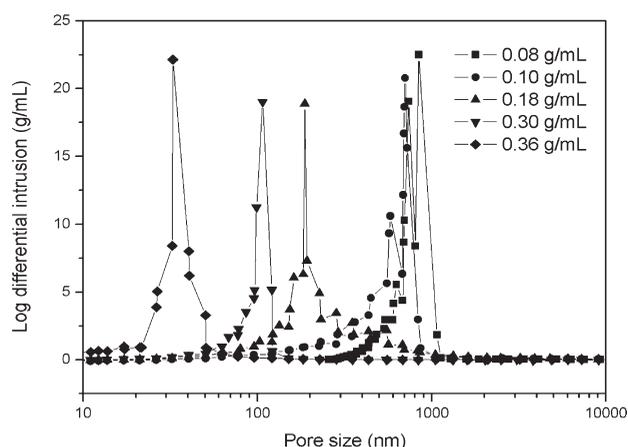


Figure 3 The pore size distributions of these phenolic foams produced at 3.0 MPa (pressure) and different resin concentrations.

and different resin concentrations. The pore size decreases and the pore structure changes more uniform with the increase of resin concentration. Figure 3 shows the pore size distributions of these foams produced at 3.0 MPa and different resin concentrations. The effects of resin concentration on the bulk densities and mean pore sizes of these phenolic foams are shown in Table II. From Figure 2, 3 and Table II, it can be seen that the pore structure of the phenolic foams can be effectively controlled by changing the resin concentration for foaming. Bulk density increases with the increase of resin concentration. The mean pore size decreases with the increase of bulk density. The bulk density increases from 0.12 to 0.50 g/cm³, and the mean pore size decreases from 800 to 30 nm with the increase of the resin concentration from 0.08 to 0.36 g/mL. At the same time, the foam prepared at high resin concentration has a better pore size distribution than that prepared at low resin concentration.

The control of resin concentration on pore structure results from the fact that the resin concentration plays an important role in nucleation and growth of bubbles. According to the theories of molecular cluster model¹³ and heterogeneous nucleation model¹⁴ in polymer solution, the nucleation and growth of bubble depend on the ambient pressure, temperature, and resin concentration. The amount of solvent

TABLE II
The Bulk Densities and the Mean Pore Sizes of these Phenolic Foams Produced at 3.0 MPa (pressure) and Different Resin Concentrations

Samples	Resin concentration (g/mL)	Bulk density (g/cm ³)	Mean pore size (nm)
F08-3.0	0.08	0.12	800
F10-3.0	0.10	0.13	700
F18-3.0	0.18	0.27	200
F30-3.0	0.30	0.40	100
F36-3.0	0.36	0.50	30

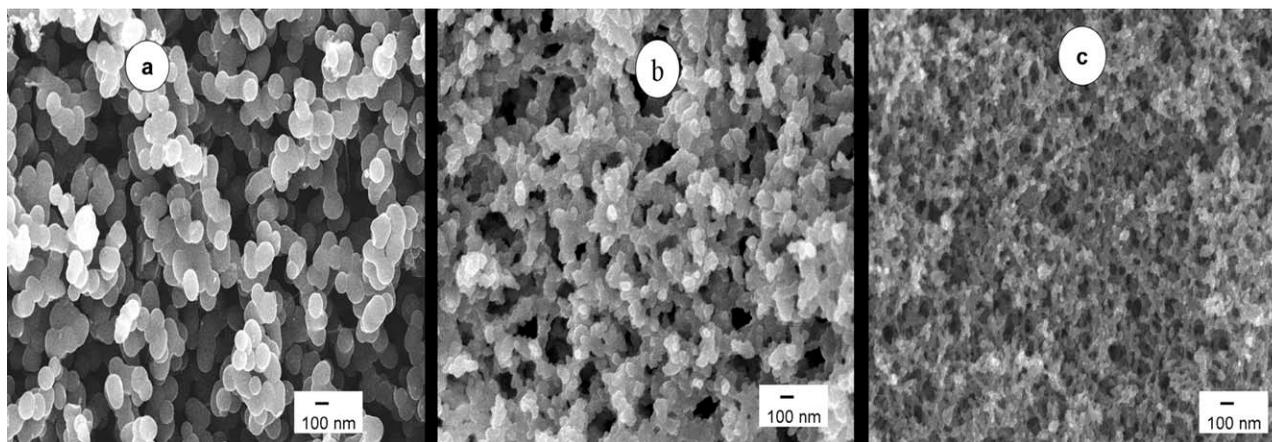


Figure 4 SEM microphotographs of these phenolic foams produced at 0.18 g/mL (resin concentration) and different pressures: a, 2.0 MPa; b, 3.0 MPa; c, 4.0 MPa.

decreases with the increase of resin concentration, which results in the decrease of the solubility of gas and the density of bubbles dissolved in the solution at constant temperature and ambient pressure. On the other hand, the rate of bubble growth depends on the gas diffusivity, which in turn depends on the rheological properties. The viscosity increases and rheological property of solution declines with the increase of resin concentration. The viscoelastic stress has much more resistance to bubble growth than interfacial stress.¹⁴ The high viscosity and poor rheological properties dampens the diffusion of gas in solution and the incorporation of bubble to form bigger bubble. Hence, nucleated bubbles experience large resistance due to high resin concentration, resulting in smaller bubble size.^{15,16}

Effect of the pressure on the pore structure

Figure 4 shows the SEM images of these foams produced at 0.18 g/mL and different pressures. From

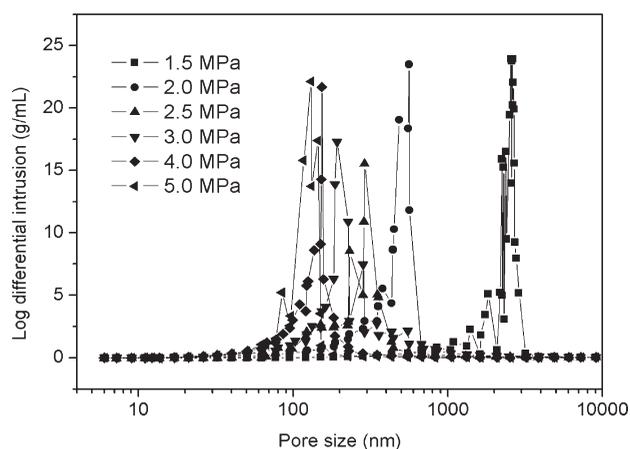


Figure 5 The pore size distributions of these phenolic foams produced at 0.18 g/mL (resin concentration) and different pressures.

Figure 4, it can be seen that the pressure has an obvious effect on the pore structure of the produced foam. The pore size decreases and the pore structure changes good with the increase of pressure. Figure 5 shows the pore size distributions of phenolic foams produced at 0.18 g/mL and different pressures. The effects of pressure on the bulk densities and mean pore size of phenolic foams are shown in Table III. The mean pore size decreases from 2.0 μm to 145 nm, and the bulk density increases from 0.15 to 0.33 g/cm^3 with the increase of pressure from 1.5 to 5.0 MPa. It indicates that the pore structure of the phenolic foam can be effectively controlled by changing the pressure for foaming. But, the optimal range of the pressure is from 2.0 to 4.0 MPa. When pressure is lower than 2.0 MPa (for example at 1.5 MPa, PF18-1.5), the produced sample has a poor pore structure (inhomogeneous distribution and big average pore size of 2.0 μm), resulting in poor properties). And when pressure is higher than 4.0 MPa (for example at 5.0 MPa, PF18-5.0), the produced sample has similar pore structure and bulk density with that produced at 4.0 MPa.

The pore structure of phenolic foam is attributed to the foaming of ethanol. In this study, the resin solution is heated to foam in an autoclave under

TABLE III
The Bulk Densities and the Mean Pore Sizes of these Phenolic Foams Produced at 0.18 g/mL (Resin Concentration) and Different Pressures

Samples	Pressure (MPa)	Bulk density (g/cm^3)	Mean pore size (nm)
F18-1.5	1.5	0.15	2000
F18-2.0	2.0	0.17	600
F18-2.5	2.5	0.25	300
F18-3.0	3.0	0.27	200
F18-4.0	4.0	0.32	150
F18-5.0	5.0	0.33	145

TABLE IV
The Typical Properties of the Phenolic foams Produced and a Comparison with those Phenolic foams Reported by Literatures

Samples	Bulk density (g/cm ³)	Compressive strength (MPa)	Specific strength (MPa/(g/cm ³))	Thermal conductivity (W/m·K)
F08-3.0	0.12	1.03	8.58	0.028
F10-3.0	0.13	1.18	9.08	0.031
F18-2.0	0.15	1.24	8.27	0.032
F18-2.5	0.21	1.89	9.00	0.053
F18-3.0	0.27	2.49	9.22	0.055
F18-4.0	0.32	3.26	10.19	0.058
Carvalho et al. ¹¹	0.12	0.80	6.67	0.057
Shutov ¹²	0.25	2.10	8.40	0.057

different ambient pressure, which has a main effect on the nucleation and growth of bubble. According to the theories of molecular cluster model¹³ and heterogeneous nucleation model¹⁴ in polymer solution, large numbers of bubbles are nucleated at high ambient pressure. And high ambient pressure allows the bubbles to attain steady-state configuration very rapidly. The trends of bubble growth indicate that an increase in the ambient pressure results in a smaller equilibrium cell (bubble) radius. According to the interfacial kinetic and Laplace equation of bubble, the radius of bubble can be obtained from the force balance (between gas pressure inside bubble, ambient pressure, and surface tension) at the bubble interface. A conclusion can be obtained that the pressure inside bubble increases with the increase of ambient pressure at same condition. It is well known that the pressure inside bubble has an inverse ratio relation with the radius of the bubble.¹⁵ So, high pressure results in smaller bubble size and good pore structure.

Compressive strength and thermal conductivity of the phenolic foam

The typical properties of these phenolic foams prepared and a comparison with those phenolic foams reported by literatures are shown in Table IV. It can be seen that the compressive strength of the prepared foam is higher than the conventional phenolic foam and thermal conductivity of the prepared foam is lower than the conventional phenolic foam with similar density.^{11,12} For example, thermal conductivity of phenolic foam (PF08-3.0, 0.12 g/cm³) is lower than conventional phenolic foam (0.12 g/cm³, 0.057 W/mK)¹¹ and closes to the phenolic foams (0.012 g/cm³, 0.029 W/mK) with closed-cell structure at skin derived from novel microwave foaming.¹⁷ Compressive strength of the phenolic foam (PF18-4.0, 0.32 g/cm³) reaches up to 3.26 MPa, and its thermal conductivity is only 0.058 W/mK.

The improvement of the compressive strength and thermal insulation properties is attributed to that the

foam has a good nanometer pore structure. The mechanical and thermal properties of porous polymer materials are significantly affected by the pore structure.^{18,19} During compressive loading, nanometer pore helps to scatter and absorb the stress and energy for keeping the integrity of skeleton, which ensures the material high strength and modulus. For thermal insulation, nanometer pore can more effectively inhibit the heat transfer through the material. So, the phenolic foam with nanometer pore structure has better compressive strength and thermal insulation than that with micrometer pore structure.

CONCLUSION

In conclusion, by adopting the novel foaming method of phenolic resin solution under pressure (2.0–4.0 MPa), the phenolic foam with good nanometer pore structure, high compressive strength, and low thermal conductivity was prepared. The nanometer pore structure greatly improves the compressive strength and thermal insulation properties of the phenolic foam and can be effectively controlled by changing the resin concentration and pressure for foaming. Pore size changes small with the increase of resin concentration or pressure. The effects on pore structure are attributed to that the nucleation and growth of bubble depend on the pressure and resin concentration. Due to the decreases of the solubility and diffusivity of gas and the incorporation of bubbles, high resin concentration results in smaller bubble size and good distribution. Because large numbers of bubbles nucleate and form steady-state configuration very rapidly, high pressure results in smaller bubble size and good distribution. The range of optimal pressure is 2.0–4.0 MPa, at which the sample has nanometer pore size.

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