



Investigation of the effect of sol concentration on the microstructure and morphology of Novolac hyperporous



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ABSTRACT

Novolac hyperporous materials were successfully synthesized using sol–gel polymerization of Novolac resin with hexamethylenetetramine (HMTA) catalyst in the solvent vapor saturated atmosphere, followed by subcritical drying. Mercury porosimetry results showed that these materials had large pore volume, more than 1 cm³/g. SEM micrographs showed that these materials formed strongly cross-linked aggregates. Therefore, these results demonstrated that these materials would be termed as hyperporous materials.

Novolac hyperporous materials can be either crushed or invaded by mercury during mercury porosimetry experiments. In this work, six samples with different initial sol concentration were examined. It has been shown here that a sample with higher porosity exhibited two volume variation mechanisms successively; compaction followed by intrusion, when submitted to mercury porosimetry that real result could be obtained by applying Pirard's collapse model below the pressure of transition, P_t , and Washburn's intrusion theory above P_t . Low porosity sample showed the collapse under mercury pressure only and no transient pressure could be observed. It means mercury does not penetrate the pore network, but the whole material is densified. Microstructure of these hyperporous materials directly influences mechanism changing from collapsing to intrusion.

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1. Introduction

Microstructure hyperporous organic materials are obtained from highly cross-linked organic gels. These materials exhibit ultrafine pore sizes, continuous porosity, high specific surface area, and a microstructure with characteristic diameters of about 10 nm [1,2]. The name of this microstructure hyperporous material comes from Pirard definition which are materials with common characteristic properties, such as large pore volume and strongly cross-linked aggregates, made of small size particles gathered up in filament-shape [3]. In some cases, because of nanoscale of pore size, we could specially call them nanostructure hyperporous materials. One of the most famous hyperporous materials are organic and carbon aerogels which were synthesized by Pekala [4].

How to prepare microstructure hyperporous materials with a competitive price-to-performance ratio is currently an active research area. The main challenges for making these materials as commercial products have two aspects: on one hand, conventional process involves long gelation time and high cost of supercritical drying device and on the other hand, high cost of raw materials, especially expensive resorcinol. Many efforts have been made to explore the cheap raw materials [5–9]. Many researches have been made in order to simplify the preparation process [10–13]. Main disadvantage of these methods is long preparation time; preparation temperature should be lower than

standard boiling point of the solvent. The low polymerization temperature is used to prevent solvent evaporation and solution blowing. Conducting sol–gel polymerization at low temperatures has two defects; one is that the low temperature sol–gel polymerization leads to slow curing reactions and hence, long required time for preparation of organic gel another, the low temperature sol–gel polymerization leads to low cross-link density [10].

Materials like polymeric hyperporous exposed to mercury porosimetry, show two different behaviors. The pore size distribution was determined by Pirard's collapse model [14,15] below pressure of transition (P_t) and by Washburn's intrusion theory [16] above P_t . The behavior of these samples is identical to that of silica xerogels [8] and Resorcinol–Formaldehyde aerogel [17], which means they are densified without intrusion when the pressure is less than P_t and penetrated by mercury without volume change when the pressure is higher. For calculating pore distribution above P_t , Washburn equation is used as follow:

$$r = \frac{2\gamma \cos\theta}{P} \quad (1)$$

where r is the cylindrical pore radius, P is the pressure at which mercury penetrates into the pore, γ is the surface tension of mercury (0.485 N/m) and θ is the contact angle between the mercury meniscus and a flat non-metallic surface ($\theta \approx 140^\circ$).

During densification, mercury isostatic pressure crushes pores whose sizes exceed a limit size L entirely, being L a function of the

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pressure P . Pores smaller than the limit size remain unaffected. The relation between L and P has been determined as Pirard's equation:

$$L = \frac{k_f}{P^{0.25}} \quad (2)$$

Eq. (2) expresses the buckling mechanism. It relates the length of chain-like aggregates between two branching points, L , to pressure P and k_f constant which should be experimentally determined for each material.

For samples that show transient pressure, at pressure P_t both Eqs. (1) and (2) are simultaneously valid when $L = 2r$. It allows computing the value of the buckling constant k_f using Eq. (3):

$$k_f = \frac{4\gamma \cos\theta}{P^{0.75}} \quad (3)$$

The values of the buckling constant k_f are in Table 1.

In this work, high temperature–pressure sol–gel polymerization of Novolac resin under 2-propanol saturated atmosphere are described in more details since it was prepared in our laboratory [18]. Naseri et al. [18] prepared the organic gel at temperatures higher than boiling point of solvent and investigated the effect of solvent on drying shrinkage. The results showed that an increase of solvent polarity increased the capillary pressure on the gel, and more shrinkage was observed.

This paper focuses on the morphological study of these microstructure hyperporous materials by using mercury porosimetry and scanning electron microscope (SEM) to determine the details of microstructure changes within the organic network upon changing the concentration of initial sol in sol–gel polymerization.

2. Experimental

In this work, a sol–gel polymerization of Novolac type phenolic resin with hexamethylenetetramine (HMTA) was applied to synthesis microstructure hyperporous materials. Also, a high temperature–pressure polymerization under saturated atmosphere of vapor of solvent was developed. This polymerization condition helps us to dominate the restriction of sol–gel polymerization temperature [18]. Solvent vapor saturated atmosphere could affect preparation process of gel through three different mechanisms. First, it prevents the removal of solvent inside the sol. Second, the saturation pressure acts like a mechanical press and prevents resin blowing as a consequence of rapid releasing of volatile by-products in a short period of time. Finally, the elevation of boiling point as a consequence of increasing surrounding pressure hinders boiling of solvent inside the sol. Therefore, rising curing temperature reduced the required time for preparation of organic gels from 5 days to lower than 6 h.

On the basis of sol–gel polymerization, the synthesis of monolithic organic gels has been explored to elaborate monolithic microstructure sample, after a drying step, for further preliminary structural characterization. The sol–gel route used here is based on the polycondensation polymerization of Novolac resin with HMTA activator, leading to a 3D network with high degree cross-linkage.

According to Table 1, six samples with different concentrations of Novolac in initial sol were prepared. Mixture of Novolac resin with HMTA was first dissolved in a suitable organic medium that uses 2-propanol, where both the Novolac oligomer and HMTA were soluble. Subsequently, the resulting solution was transferred to mold and then the mold was placed in an autoclave filled with pure solvent which provides saturated atmosphere of solvent vapor and curing of the Novolac solution took place for 6 h at 120 °C. The resulting gel was dried at ambient pressure during 24 h at room temperature then 24 h at 90 °C and 24 h at 120 °C. At the end of process, for making sure about curing of Novolac, the gel was heated at 140 °C for 4 h.

Characterization was performed on dry gels. The bulk density of the nanostructure was classically calculated. Mercury porosimetry was performed from 0.01 to 200 MPa using an instrument of PASCAL 440 Thermo Finnigan, Italy. The morphology of microstructure was also observed using FESEM (TESCAN, MIRA model, Republic of Czech). The sizes of interconnected domains in the gels were evaluated by averaging more than 20 directly measured thicknesses Novolac microstructure skeletons on the SEM photographs.

Compressive tests were carried out using electronic universal testing machine (Gotachi, Taiwan). The sample machined into cylinder solids with dimensions of 34 mm diameter by 17 mm height according to ASTM D 1621. The tests were run with a displacement rate of 1 mm/min.

3. Results

Mercury porosimetry is the most attractive method to determine the pore and pore size distribution [14]. Two different behaviors were observed on various samples. Samples with lower concentration in the initial sol (with higher porosity) had a non-classical behavior when exposed to mercury porosimetry pressure, as shown in Fig. 1. Under isostatic pressure, two successive behaviors may be exhibited. At low pressure, the sample collapses under mercury pressure and above a pressure of transition (P_t), mercury can enter the network of small pores without being destroyed during the compression at low pressure. P_t was observed by sudden change of slope of volume versus pressure curve and this critical pressure divided the curve into two distinct parts. P_t was estimated 0.2, 0.6, 1.5 and 6 MPa for N10, N15, N20 and N25 samples, respectively. Due to the fragmentation of these samples during mercury extrusion, weighting and size measurement could not be done but it is obvious that the intrusion–extrusion is the acceptable mechanism to explain the volume variation above the P_t pressure. The samples with lower porosity, N30 and N35, only collapse under mercury pressure and no volume variation is observed when the pressure decreases and also no transient pressure could be seen, as shown in Fig. 2. The whole pore size distribution was determined by Pirard's collapse equation.

Using the suitable equation, pore volume distributions versus pore size can be determined for each sample (Figs. 1(b), (c), (d), (f) and 2(b)). Consequently, the N30 and N35 sample's mercury porosimetry data should be analyzed by the Pirard's collapse (Eq. (2)). Their distributions show that these samples contain only pore size below 54 and 36 nm, respectively. SEM observations proved that the results obtained from Eq. (2) are correct, whereas calculation of pore size using Eq. (1)

Table 1
Sample composition and properties.

Sample	Novolac concentration in sol (wt.%)	ρ_b (± 0.002 g/cm ³)	d (μ m)	P_t (MPa)	k_f (nm MPa ^{0.25})	Compression strength (MPa)
N10	10	0.104	2.32	0.2	4969	–
N15	15	0.165	0.54	0.6	2180	–
N20	20	0.261	0.26	1.5	1096	1.58
N25	25	0.312	0.12	6.0	388	2.76
N30	30	0.394	0.093	>148	<21	9.73
N35	35	0.463	0.07	>200	<28	28.97

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