The buckling deformation and mechanical properties of aerogels prepared with polyethoxydisiloxane

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ABSTRACT

The high-polymeric degree or molecular-weight of self-made polyethoxydisiloxane (PEDS) was successfully used to synthesize aerogels with several advantageous mechanical characteristics, compared with those based on conventional tetraethylorthosilicate (TEOS) aerogel preparation methods. The first advantage is their lower initial values of bulk modulus (K_0), compared with those prepared via the *two-step* method; this is due to release of internal stress during the shrinkage of wet gel. Secondly, a collapse index n of -0.125 is obtained by the collapse law; this implies a new buckling destruction model. This is different from those prepared via the *two-step* method, and suggests that a hierarchical filament structure, formed by the connection of nano-particles, constitutes the solid skeleton of pores. In this paper, average aerogel pore sizes between 16.0 and 39.3 nm are analyzed by the combination of Mercury Intrusion Porosimetry (MIP) and Nitrogen Adsorption–Desorption (NAD). The microstructure and morphology of the aerogels are demonstrated by Transmission Electron Microscopy (TEM) and Field Emission Scan Electron Microscopy (FE-SEM).

1. Introduction

Aerogels were discovered more than eighty years ago, and exhibit many interesting properties, such as very high porosities, low apparent densities, high specific surface areas, and good texture stability during heat treatment at high temperatures. There is significant interest in the large scale free-cracking aerogels. The first contemporary large scale application of silica aerogels took place in high energy particle physics in the form of Cerenkov detectors. More recently, the large scale free-cracking aerogels have been demonstrated to have application in transparent super-thermal insulating windows [1]. However, the expensive production cost and poor mechanical properties restrict the widespread application of aerogels. Usually, tetramethyl orthosilicate (TMOS) and tetraethoxysilane (TEOS) as the silicon source are used to preparing silica aerogels. There are two methods [2,3] for aerogels synthesis. In the *one-step* method, all the reactants along with the catalyst are mixed in one step. Thus, the hydrolysis and condensation of the silicon alkoxide takes place simultaneously, forming a solid network. In the *two-step* method, the hydrolysis and condensation reactions are performed separately by adjusting the amount of water needed during each step of the reaction. These aerogels are prone to cracking because of shrinkage during the aging and drying of wet gel. Compared with the *one-step* method, the aerogels obtained by the *two-step* method exhibit free-cracking owing to an interlinked polymer-chain-like (IPCL) flexible structure [4]. The reason for IPCL structure forming in the *two-step* method is due to the 8–10 polymerization degree of polyethoxydisiloxane (PEDS) [5]. Consequently, new attention has been given to preparation of monolithic aerogels directly by the high polymerization degree of PEDS as the silicon source [6–8]. Studies have been reported on the gelation mechanism [9,10], structure and morphology [11,12], optical properties [13], and thermal properties of aerogels [9] based on PEDS. Further, Wong et al. [14] discussed the mechanical properties of monolithic silica aerogels made from PEDS using a universal materials testing machine. However, a systematic study regarding the relations between skeleton structure and mechanical properties of aerogels is needed. Previously, Pekala et al. [15] noted that the pores of *two-step* aerogels hierarchically collapse with increasing pressure due to the buckling deformation of the solid skeleton of aerogels; they obtained a collapse law index n of -0.25 using Mercury Intrusion Porosimetry

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(MIP). Thus far no researching about aerogels prepared by PEDS has been published.

In this paper, the goal was to summarize the novel buckling deformation of the solid skeleton of aerogels prepared by PEDS. We demonstrate and discuss the effects of the ratio of H_2O/PEDS, density and aging conditions, *etc*., on the bulk modulus of aerogels prepared by PEDS. Further, a new pore structure feature was obtained and an anti-pressure mechanism proposed. Nitrogen Adsorption–Desorption (NAD) is one of the many methods currently used to characterize the texture of porous materials, however it is commonly observed that much of the pore volume is not detected by NAD; the undetected volume is attributed to macropores. Unlike NAD, MIP can take into account the macropores. In this paper, the pore size distribution of aerogels is obtained by joint analysis of MIP and NAD. The microstructure and morphology of the aerogels were characterized by TEM and FE-SEM.

2. Experiments

2.1. Preparation of silica aerogels

As a precursor, polyethoxydisiloxane (PEDS) was synthesized according to a reported procedure [16]. In our investigations, PEDS was synthesized as follows: tetraethylorthosilicate (TEOS), ethanol, H_2O and hydrofluoric acid (HF) as catalyst were mixed with a molar ratio of 1:6:1.2:0.05 under mechanical stirring. The solution was kept at 4–5 °C for 15 days, and an average molecular weight of 2.5×10^4 g/mol (see SM, Fig. 1S) was obtained by removing the ethanol under a pressure of 2 kPa. The wet gels (Samples X and Y) were prepared by two processes: (1) the cross-linked gel was formed with insufficient water. PEDS, ethanol, H_2O and HF were mixed by varying the molar ratio of ≡Si— of PEDS/H_2O (r). This was done by establishing the weight ratio of PEDS/ethanol (w), and maintaining 0.05 M of HF in the mixture; the mixture then was poured into a 100 mL round Teflon beaker and kept for 3 days at room temperature. (2) The crosslinked gel was aged with different volume ratios of ethanol/H_2O (v) for 3 days. The sample C-1 was prepared by the *two-step* method, in which the total molar ratio of TEOS/H_2O/ethanol/HCl/NH_4OH was equal to 1:4:4:10^{-3}:5×10^{-3}. In the first step, TEOS was hydrolyzed in a solution with molar ratio of TEOS/H_2O/ethanol/HCl set at 1:1:4:10^{-3} under reflux for 1 h at 50 °C. In the second step, this solution was mixed with the remaining water and NH_4OH under mechanical stirring, and then was poured into a 100 mL round Teflon beaker and aged for 3 days. All aged gels were washed in ethanol (five times for 24 h at 30 °C, at the volume ratio of solvent/gel 2:1) and then were supercritically dried with ethanol at a temperature of 275 °C, while holding the pressure generated by the solvent vapor at approximately 10 MPa. The details for preparation of wet gels are described in Table 1.

2.2. Characterizations

The bulk densities of the aerogels were measured from known volumes and masses. The pore size distributions of the aerogels were measured by nitrogen adsorption/desorption analysis using a Micromeritics ASAP 2020 surface area and BJH pore distribution analyzer. Mercury Intrusion Porosimetry (MIP) measurements were made using a QuantaChrome Poremaster GT-60. The morphologies of samples were observed by Field Emission Scan Electron Microscopy (FE-SEM; JSM6700F, JEOL, Japan). The samples, dispersed in ethanol, were coated on a copper grid, and then dried before carrying out Transmission Electron Microscopy (TEM; JEM-2010 UHR, JEOL, Japan).

Table 1
Preparation of wet gels of different molar ratios of ≡Si— of PEDS/H_2O and weight ratios of PEDS/ethanol under different aging solutions of the volume ratio of ethanol/H_2O.

Samples	The molar ratio of ≡Si— of PEDS/H_2O (r)	The weight ratio of PEDS/ethanol (w)	The volume ratio of ethanol/H_2O (v)
C-1	–	–	–
X-1	2:1	1:2.5	80:20
X-2		1:1.5	
X-3	1:1	1:2.5	
X-4		1:1.5	
X-5	0.5:1	1:2.5	
X-6		1:1.5	
Y-1	2:1	1:2.5	50:50
Y-2		1:1.5	
Y-3	1:1	1:2.5	
Y-4		1:1.5	
Y-5	0.5:1	1:2.5	
Y-6		1:1.5	

3. Results and discussion

The basic hypothesis of MIP usually accepted is that mercury penetrates into the empty pores without elastic compression as pressure increases. Data analysis was performed using the intrusion equation proposed by Washburn [17]. However, the aerogels have a weak compressive strength, and they undergo densification without any intrusion of mercury into the pores. As shown in Fig. 1a and b, the MIP curves are identical for Samples X and Y respectively.

Initially, the samples were pressurized to 200 MPa, and then depressurized to atmospheric pressure. The MIP data displays a large volume variation called pore volume; this is due to hierarchical collapse of pores during pressure increases, so the recorded volume variation is practically irreversible during depressurization. However, the specific volume of aerogel *vs.* a function of mercury pressure was calculated by subtracting specific pore volume variation from the initial specific volume of aerogel; the curve of the specific volume of aerogel of X-1 (▲) is shown in Fig. 2.

In general, the relationship of the specific volume variation *vs.* a function of external pressure for porous material can be described as follows [18]:

$$dP = -K(dV/V) \tag{1}$$

where V is the specific volume of the sample, and the bulk modulus, K, represents the stiffness of the material; P is pressure. As shown in the inset of Fig. 2, the compression curve expresses linear elastic deformation at low pressure less P_y; the modulus is constant (K_0), therefore it is called Hookean region. However, if the aerogel is compressed to beyond the excess threshold value P_y, the aerogel exhibits yield followed by plastic hardening (i.e., increasing modulus). In this regime, the modulus changes with the volume according to a power-law:

$$K(V) = K_0(V_y/V)^m \tag{2}$$

where K_0 is the initial modulus of aerogel and V_y is the threshold volume of aerogel from the Hookean region to power-law. The effect of a finite increase in pressure must be found by integrating Eq. (2) with K given by Eq. (3):

$$P = \begin{cases} K_0 \ln(V_0/V) & V_y \leqslant V \leqslant V_0 \\ K_0 \ln(V_0/V_y) + \frac{K_0}{m}\left[(V_y/V)^m - 1\right] & V \leqslant V_y \end{cases} \tag{3}$$

The data for samples and the parameters in Eq. (3), obtained from fitting to specific volume under the mercury isostatic pressure, are given in Table 2, and the quality of a typical fitting