



Enhanced resistance of nanocellular silica to dynamic indentation



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ABSTRACT

Compared with solids, cellular materials are more lightweight yet usually weaker due to their large porosities. In the current study, it is discovered that the dynamic penetration resistance of nanocellular silica could be effectively higher than that of solid silica when the cell size is smaller than ~100 nm. This phenomenon is attributed to the local hardening that happens when the cell size is sufficiently small and the cell collapse is sufficiently fast. The finding paves a road to the development of strong and lightweight cellular materials.

1. Introduction

Cellular materials are solids containing large volume fractions of empty cells [1,2]. They are widely applied for acoustic insulation, thermal management, catalytic reaction, drug delivery, energy storage, vibration damping, and impact and shock protection [3–7]. A few examples of cellular materials include woods [8,9], bones [10,11], carbon nanotube bundles [12], silica aerogels [13], expanded polymers [14,15], and cellular metals and ceramics [16–19]. They are more lightweight but typically softer and less penetration/indentation resistant than their solid counterparts.

According to the classical theory, the strength, Y , the hardness, H , the stiffness, E , and the toughness, K_c , of a cellular material are related to its porosity, c [1,2,20,21]:

$$(Y, H, E, K_c) \propto (1-c)^\alpha \quad (1)$$

where α is a system constant ranging from 1 to 3; all of them are independent of the cell size, d . In many applications, a low mass density, ρ , is desirable and therefore, the porosity must be maximized [22,23], which however tends to weaken the material. While in some cases using weak cellular materials is acceptable, in general the material must exhibit a sufficiently high strength/hardness; otherwise they cannot meet the increasingly high requirements on structural integrity [24]. In fact, because $\rho \propto (1-c)$ and $H \propto (1-c)^\alpha$, very often the porosity has to be sacrificed to reach the required strength/hardness; these cellular materials are bulky, heavy, and of low performance [25,26].

Over the years, people were searching for solutions of lightweight and hard/strong cellular materials. Particularly, under the most critical

loading conditions, i.e. when the material is impacted, the classical relationship of $H \propto (1-c)^\alpha$ should be broken down. A number of beneficial size effects on the nanometer (nm) scale were investigated for carbon nanotubes [27], nanopillars [28], and nanowires [29]. They have excellent strengths compared with bulk materials, thanks to the low defect density and the beneficial surface phenomena. However, they are small-sized. When they collectively form large cellular structures, e.g. carbon nanotube forests [30], the dominant deformation mechanisms would change and the nm-scale strength may not be proportionally amplified. Nanoporous gold has demonstrated a higher strength than solid gold [31,32], due to the hardening effect associated with the small ligament length; yet, this mechanism is most efficient when the network material is inherently soft and ductile. No conclusive results have been obtained for monolithic cellular materials having intrinsically hard ligaments.

2. Experimental

2.1. Sample processing

Cellular silica samples were fabricated via two sol-gel approaches [33–35]: One for average cell sizes smaller than 500 nm [33]; the other for average cell sizes on the microscopic scale. The cellular morphology was conditioned by a subcritical calcination (SCC) technique [36]. The details of sample processing have been documented elsewhere [36].

For the first sol-gel method, Sigma-Aldrich Ludox HS-40 colloidal silica and PQ Kasil-1 potassium silicate solution, with the total mass of 800 g and the mass ratio in the range from 5:95 to 40:60, were mixed together through magnetic stirring for 30 min. The larger the amount

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of the colloidal silica, the smaller the cell size would be. Next, aqueous solution of formamide (200 g, 40 wt%) was slowly added, and the stirring continued for another 30 min. After that, the solution was poured into a set of polypropylene plastic vials having the inner diameter of 36 mm and the height of 16 mm. After aging for 24 h at room temperature, the wet gels were thoroughly rinsed by a sequential solutions at $\sim 90^\circ\text{C}$: ammonium nitrate (1 M), nitric acid (1 M), and deionized water. Finally, they were washed by pure methanol at room temperature.

For the second method, Sigma-Aldrich polyethylene glycol (PEG, 32 g) with the average molecular weight of 10,000 was dissolved in aqueous solution of acetic acid (300 ml, 0.01 M). Then, tetramethyl orthosilicate (TMOS, 99%, 150 ml) ordered from Sigma-Aldrich was added under magnetic stirring. After mixing for 30 min, the solution was transported into a set of polypropylene plastic vials having the inner diameter of 46 mm and the height of 22 mm. After aging at 40°C for 3 days, the wet gels were sequentially rinsed by aqueous ammonia solution (0.1 M) at $\sim 120^\circ\text{C}$, then by nitric acid (0.1 M) and deionized water at $\sim 90^\circ\text{C}$, and eventually by pure methanol at room temperature.

In both approaches, every step of the washing process was repeated for at least five times. After that, the solid gels were vacuum dried in an oven (VWR 1330GM) at 80°C for 3 days. The obtained silica monoliths were fired in a horizontal tube furnace (MTI GSL-1700X) at selected SCC temperatures ($1200^\circ\text{C} \leq T_s \leq 1260^\circ\text{C}$) for 1 h. The initial ramp rate was set to be 3°C min^{-1} ; when the temperature was raised to 100°C below T_s , the ramp rate was reduced to 1°C min^{-1} . After SCC, the cooling rate was set as 3°C min^{-1} . Solid silica disks were employed as reference samples. They were processed through a similar procedure, but were fired at 1250°C for 12 h.

The SCC-treated silica samples were polished to remove the surface layers by a set of silicon carbide sandpapers [37,38]: 320-grit first, then 600-grit, 1200-grit, and eventually 2500-grit. Before the SCC treatment, the sample thickness was 10–14 mm; after the calcination, the thickness shrank to 7–9 mm. The sample thickness after each step of polishing was 5–6 mm, 5.0 mm, 4.75 mm, and 4.50 mm, respectively. The fabrication conditions of cellular and solid silica samples are summarized in Table 1.

2.2. Sample characterization

The porosity of cellular silica sample was defined as the percentage of volume of empty cells over the total sample volume [1]. It was calculated from the mass density: $c=1-\rho/\rho_n$, where ρ is the sample mass density and $\rho_n=2.2\text{ g cm}^{-3}$ is the density of solid amorphous silica. Through mercury porosimetry [36], the cell size was estimated from the well-established Washburn equation [36]: $d=4\sigma\cdot\cos\theta/P_{\text{Hg}}$, where $\sigma=0.484\text{ N m}^{-1}$ is the surface tension of mercury, $\theta\sim 140^\circ$ is the contact angle, and P_{Hg} is the measured mercury infiltration pressure. The measurement results of porosity and cell size are listed in Table 1.

Both cellular and solid silica samples were analyzed by a Bruker D8 Advance Diffractometer with Cu K α radiation ($\lambda=1.5418\text{ \AA}$). The scan speed was set to be 0.1 s per step; the step size was 0.02° ; the 2θ range was $10\text{--}80^\circ$. Typical x-ray diffraction curves of cellular and solid silica

samples are presented in Fig. 1a. In addition, the cellular silica samples were observed under a scanning electron microscope (SEM, FEI-XL30) at the beam energy of 20 kV and the spot size of 3.0. Prior to the observation, the SEM samples had been coated with iridium at 85 mA for 6 s by an Emitech K575X sputter coater. The cellular structures are shown in Fig. 1(b-d).

2.3. Indentation tests

In this investigation, a home-made indentation testing system was employed to conduct quasi-static and dynamic indentation tests. As shown in Fig. 2a, the indentation system included a front part, a rear part and a hemispherical indenter. The front and rear parts were made of 17-4 PH stainless steel. With their symmetrical configuration, the bending deformation of silica sample during testing could be minimized. An indenter with the diameter of 4.75 mm, the hardness of 91 HRA, and the surface roughness of 0.7 micro inch Ra maximum was used. It was firmly attached to one end of a 17-4 PH stainless steel cylinder by VISHAY M-Bond 200 adhesive. The diameter and the length of the cylinder were 12.7 mm and 25.4 mm, respectively. A silica sample was sandwiched in between the indenter and the steel substrate on the rear part, as illustrated in Fig. 2b. The far end of the steel cylinder would be subjected to either a quasi-static or an impact loading. The lateral surface of the silica sample was confined by two rings: a compliant polyurethane (PU) inner ring, with the initial inner diameter of 19.1 mm and the initial outer diameter of 22.2 mm; and a stiff polyvinyl chloride (PVC) heat-treated outer ring, with the initial inner diameter of 25.4 mm and the shrinking ratio of 2:1.

Quasi-static indentation tests were conducted by compressing the hemispherical indenter into the sample surface using an Instron 5582 machine, as illustrated in Fig. 3a. The loading/unloading rate was 0.01 mm min^{-1} , and the peak loading force was 300 N. Typical force-displacement curves are shown in Fig. 3b. For each type of silica, at least three samples were tested.

An impact system, as illustrated in Fig. 4a, was employed to provide dynamic indentation and compression loadings [7,39–41]. The details of the impact system and the results of dynamic compression tests have been documented in Supplementary material. A titanium (Ti) tube striker with the total mass of 63 g was projected from a high-pressure gas chamber to impact a stainless steel (17-4 PH H900) incident bar. The striker speed was measured to be $\sim 8.5\text{ m s}^{-1}$ for all the tests by a set of photomicro sensors (OMRON EE-SPW421). The incident bar then compressed a hemispherical indenter into the silica disk sample. The silica sample was firmly supported by a stainless steel substrate, followed by the transmitted bar. The diameter of the indenter was 4.75 mm. The diameters of the incident and the transmitted bars were the same 12.7 mm. Two sets of strain gauges (Vishay WK-13-250BF-10C) were mounted at the center of the two bars respectively to record stress wave profiles through a data acquisition system (Vishay 2310B). Typical incident and transmitted stress wave profiles are shown in Figs. 4b and 4c, respectively. The loading mode was similar with that of the quasi-static indentation experiment, while the loading rate was much higher. For each type of silica, at least three samples were tested.

Table 1

Synthesis parameters and properties of cellular and solid silica samples.

Mass ratio of reagents	TMOS to PEG	Colloidal silica to potassium silicate							
		5:95	10:90	15:85	18.5:81.5	25:75	30:70	40:60	25:75
SCC temperature [$^\circ\text{C}$]	1210	1249	1254	1247	1236	1236	1229	1224	1250 (12 h)
Sample thickness [mm]	4.52 ± 0.01	4.54 ± 0.01	4.53 ± 0.01	4.54 ± 0.01	4.53 ± 0.01	4.54 ± 0.01	4.53 ± 0.01	4.54 ± 0.01	4.54 ± 0.01
Cell size range [nm]	[390,1010]	[210,340]	[170,250]	[135,200]	[120,170]	[90,120]	[70,90]	[40,60]	Solid silica
Average cell size [nm]	700 ± 440	275 ± 90	210 ± 60	165 ± 45	145 ± 35	105 ± 15	80 ± 15	50 ± 10	Solid silica
Porosity [%]	59.7 ± 1.0	60.7 ± 1.2	59.9 ± 0.6	59.8 ± 1.2	60.6 ± 1.1	61.4 ± 1.4	60.5 ± 0.5	60.5 ± 0.5	< 1.0

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