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Mechanical Properties of Silica Aerogel – A Molecular Dynamics Study

Jincheng Lei[1)], Jianying Hu[2)] and *Zishun Liu[3)]

[1), 2)] *Int. Center for Applied Mechanics; State Key Laboratory for Strength and Vibration of Mechanical Structures, Xi'an Jiaotong University, Xi'an, 710049, China*
zishunliu@mail.xjtu.edu.cn

ABSTRACT

Aerogels, the ultra-light materials which can be even just slightly heavier than air, have drawn much attention due to its superior thermal, acoustical and mechanical properties. In this paper, Molecular Dynamics (MD) is adopted to investigate the mechanical properties of bulk silica aerogel. The nano-structure of silica aerogel is constructed by a heating, expanding and cooling method, which results in the reasonable uniform porous structure with different densities ranging from 0.3g/m^3 to 1.0g/m^3. The Young's modulus and Poisson's Ratio are obtained by uniaxial and biaxial tension tests. Firstly, we find that Young's modulus of the nano-porous structures turns out to be affected by the density in a power law with the parameter of 3.32, which is in agreement with the earlier experimental and simulation results. For Poisson's ratio, we have observed that the value is also affected by density, exhibiting that the Poisson's ratio decreases with the increasing of density from 0.3g/cm^3 to 0.75g/cm^3, while the value of 0.33 can be adopted for the density ranging between 0.8g/cm^3 and 1.0g/cm^3. Assuming bulk silica aerogel to be a homogenous material, the mechanical properties may be described by these two parameters, i.e. Young's modulus and Poisson's ratio. Thus, the constitutive relation of silica aerogel whose density is from 0.3g/cm^3 to 1.0g/cm^3 has been preliminarily proposed in this study.

Keyword: Silica aerogel, Molecular Dynamics, Young's modulus, Poisson's ratio, Constitutive relation

1. INTRODUCTION

Silica aerogels are nano-porous materials with a very large surface-to-volume ratio. Due to the excellent thermal, optical, acoustical and mechanical properties, it has been widely used to thermal and acoustical insulator, solar energy collector and so on. Silica aerogel is often prepared by the sol-gel process followed by the supercritical drying(Murillo et al. 2010). Many experiments, such as small-angle x-ray scattering (SAXS) and helium pycnometry (Fricke and Tillotson 1997; Woignier and Phalippou 1990), have demonstrated that silica aerogels possess the fractal structures, in other

[1) ,2)] Postgraduate Student
[3)] Professor

words, the nano-porous structures span many hierarchical regimes (Nakano et al. 1993). The SEM image of prepared silica aerogel shows that it consists of open pores and the backbone which is a network of gel particles (Zhao et al. 2013). At the same time, the backbone particles are also the nano-porous structures whose pore size is much less than that in the SEM image. It means that taking the fractal structures into account for silica aerogels may lead to a more accurate description.

Molecular dynamics simulations have been adopted to investigate the geometrical, thermal and mechanical properties by many researchers (Murillo et al. 2010; Nakano et al. 1993; Ng et al. 2012; Pohl et al. 1995). To generate the MD model of silica aerogel, Kieffer (Kieffer and Angell 1988) firstly proposed the negative pressure rupturing method, i.e. expanding a sample of silica gradually to the wanted density. However, as the Born-Mayer potential, a two-body interaction, was chosen to be the interactive potential of the Si and O atoms, this method resulted in stable nanoporous structures only in a small range of density. Murillo et al. (Murillo et al. 2010) improved the negative pressure rupturing method by expanding the sample of silica instantaneously to the wanted density using more atoms. In this study, we use similar method with Murillo et al to construct the simulation model. From the previous experimental study on the mechanical properties of silica aerogel (Murillo et al. 2010; Woignier et al. 1989; Woignier et al. 1998), it was proved that the Young's modulus of silica aerogel is in a power-law relation with the density. To obtain the mechanical properties of silica aerogels, we proposed an approach to measure the Young's modulus and Poisson's ratio in different densities. Since the macroscopic mechanical properties of silica aerogels will be more useful for new aerogel product design and engineering application, we try to use molecular dynamics simulation results to generate the macroscopic constitutive relation of silica aerogels.

2. Method

To investigate the mechanical properties of silica aerogel, LAMMPS is employed to generate porous samples of silica aerogels and to perform the uniaxial and biaxial tension test for determining Young's modulus and Poisson's ratio of silica aerogels. In present study, we construct five different atomic models in every increment of 0.05 g/cm^3 ranging from 0.3 g/cm^3 to 1.0 g/cm^3 for more accurate quantitative properties.

2.1 Molecular dynamics settings

There are a few kinds of interatomic potentials for the molecular dynamics simulations of silica aerogels, such as one developed by Vashishta et al. (Vashishta et al. 1990) and BKS potential (Beest et al. 1990). In this study, we adopt the re-parameterized Tersoff potential (Ng et al. 2012) for Silicon and Oxygen atoms to carry out our simulations. The mathematical form of the potential is as follows:

$$E = \sum_i E_i = \frac{1}{2}\sum_{i \neq j} V_{ij}$$

$$V_{ij} = f_c\left(r_{ij}\right)\left[\, f_R\left(r_{ij}\right) + b_{ij}\, f_A\left(r_{ij}\right)\right]$$

$$f_R(r_{ij}) = A_{ij}\exp(-\lambda_{ij} r_{ij})$$

$$f_A(r_{ij}) = B_{ij}\exp(-\mu_{ij} r_{ij})$$

$$f_c(r_{ij}) = \begin{cases} 1, r_{ij} < R_{ij} \\ \frac{1}{2} + \frac{1}{2}\cos(\pi \frac{r_{ij} - R_{ij}}{S_{ij} - R_{ij}}), R_{ij} < r_{ij} < S_{ij} \\ 0, r_{ij} > S_{ij} \end{cases} \quad (1)$$

$$b_{ij} = \chi_{ij}(1 + \beta_i^{n_i}\zeta_{ij}^{n_i})^{-1/2n_i}$$

$$\zeta_{ij} = \sum_{k \neq i,j} f_c(r_{ik})\omega_{ik} g(\theta_{ijk})$$

$$g(\theta_{ijk}) = 1 + c_i^2 / d_i^2 - c_i^2 / [d_i^2 + (h_i - \cos\theta_{ijk})^2]$$

$$\lambda_{ij} = (\lambda_i + \lambda_j)/2, \mu_{ij} = (\mu_i + \mu_j)/2$$

$$A_{ij} = (A_i + A_j)^{1/2}, B_{ij} = (B_i + B_j)^{1/2}$$

$$R_{ij} = (R_i R_j)^{1/2}, S_{ij} = (S_i S_j)^{1/2}$$

where i, j, and k the atomic labels, r_{ij} the distance between atoms i and j, θ_{ijk} the bond angle between bonds ij and jk, χ_{ij} a parameter for strengthening/weakening heteropolar bonds, such that χ_{S_i-O} accounts for the charge transfer between Si and O atoms.

2.2 Preparation of porous samples

The method developed by Kieffer et al. (Kieffer and Angell 1988), which is called negative pressure rupturing method, was firstly used to generate the porous structures by expanding the sample of silica gradually. Since the shortcoming of the usable range of density, it was improved by Murillo et al. (Murillo et al. 2010), where samples of silica are expanded instantaneously at the room temperature. From our study, we notice that it is unstable to obtain a reasonably uniform porous structure using Murillo's improved process of expanding, heating and quenching when the density of silica aerogel is above 0.8 g/cm^3, while it works well when the density is lower than 0.8g/cm^3. In present study, we change the sequence of the simulation process, i.e. heating, expanding and cooling, , and we find that the proposed new method can perform very well when the density ranges from 0.3 g/cm^3 to 1.0g/cm^3. In this approach, firstly, the sample of bulk silica is relaxed and heated from 300K to 3000K. Then it is relaxed once again,

expanded to the target density instantaneously and relaxed in the atmosphere of 3000K to generate the preliminarily porous structure. Finally, the sample is cooled down to the room temperature 300K to obtain the stable geometry. To obtain more accurate results, we construct five models in every increment of 0.05 g/cm^3 ranging from 0.3 g/cm^3 to 1.0 g/cm^3, i.e. total 15 samples of different densities are selected.

2.3 Mechanical characterization

In order to investigate the mechanical properties of these samples, uniaxial and biaxial tension tests (Riccardi et al. 2012) are simulated to measure the Young's modulus and Poisson's ratio respectively. The power-law relation between the Young's modulus and the density is reproduced in our results. Besides, we find that the Poisson's ratio of these porous samples is also in a power-law relation with the density.

In the uniaxial tension test, a strain rate of 0.0001 ps^{-1} is imposed in the x-direction of the sample for 200 ps. This small strain of 0.02 guarantees eliminating the influence of the density changing effectively. The Young's modulus is determined by the slope of the stress-strain curve.

Poisson's ratio of model is measured by the biaxial tension test. In Molecular Dynamics simulations, a uniaxial tension test for a cubic material, especially for the non-homogenous material, usually produces the different deformation in the other two directions, leading to different components of Poisson's ratio. If we want to study the bulk mechanical properties of this kind of materials assuming its homogeneity, a biaxial tension test is a better choice. The Poisson's ratio of silica aerogels is calculated using following equation:

$$\nu = -\frac{\varepsilon_z}{\varepsilon_x + \varepsilon_y - \varepsilon_z} \tag{2}$$

3. Results and discussions

3.1 Sample preparation

The negative pressure rupturing method is verified to generate the porous structure effectively. However, it is found that the model is unstable when the density is above 0.8 g/cm^3. It may be caused by that we choose the re-parameterized Tersoff potential instead of Murillo's. On the other hand, the instability of this method may result from the unphysical procedures that expand the dense silica at the room temperature. In our work, we proposed an approach to rearrange the sequence of these procedures to improve its instability, i.e. heating, expanding and cooling. Figure 1 displays the model of silica aerogel with the density of 0.3g/cm^3 obtained by the improved method.

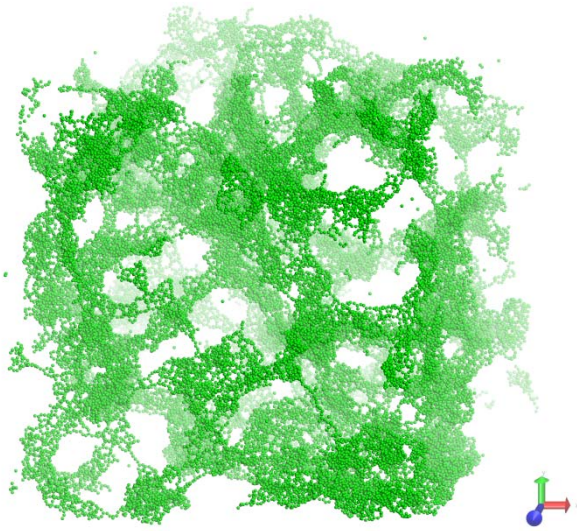

Fig. 1 The model of silica aerogels with the density of 0.3g/cm^3 using molecular dynamics

3.2 Young's modulus

Uniaxial tension tests are employed to investigate the Young's modulus with the strain rate of 0.0001 ps^{-1} and the final loading strain of 0.02. It is crucial to eliminate the sampling error while calculate the Young's modulus for the randomness of the porous structures. Thus, in our study the Young's modulus of each point of density is the average of five samples with the same density but different structure.

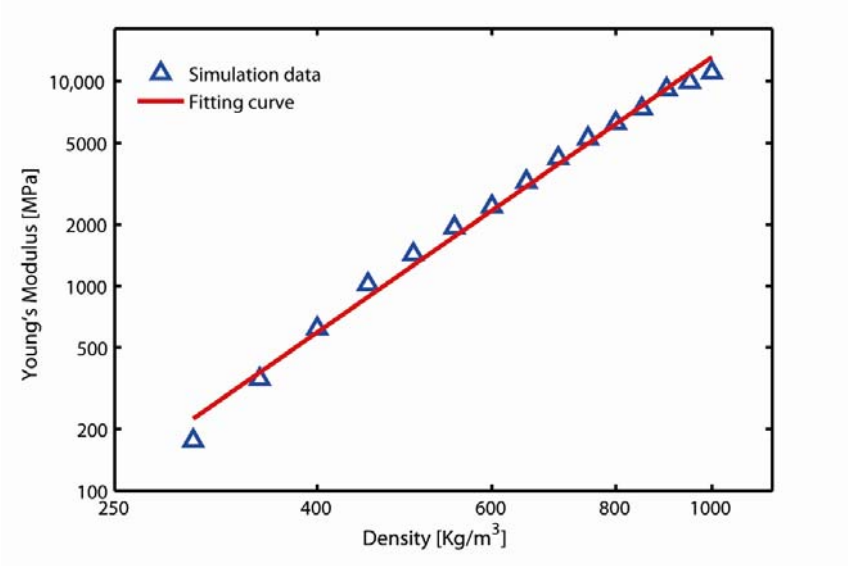

Fig. 2 The relation between Young's modulus and the density in log-log coordinate (The small triangles refer to simulation results. The red curve refers to the power-law fitting curve of simulation data.)

Figure 2 shows the simulation results and the power-law fitting curve in log-log coordinate. It has been demonstrated that the relation between Young's Modulus and density satisfies a power law by experiments and simulations. In this curve, we can find that our simulation results satisfy almost perfectly the power-law equation as follows:

$$E = 9.638 \times 10^{-7} \cdot \rho^{3.378} \tag{3}$$

where E the Young's modulus, ρ the density. The exponent of this relation is close to the results of Campbell and Murillo, which is 3.5 and 3.11 respectively (Campbell et al. 1999; Murillo et al. 2010).

3.3 Poisson's ratio

Biaxial tension tests are employed to investigate the Poisson's ratio with the strain of 0.2 in both X and Y directions. To deal with the average of the Poisson's ratio of five samples, we firstly calculate the average of ε_z, and then obtain the final value from the Eq.(2).

The relation between Poisson's ratio and the density from the simulation results and the power-law fitting curve is described in Figure 3. Although the data points have some kind scattering, it shows the coincident trend to decreasing with the density increasing compared to the power-law curve, which can be described by:

$$v = 0.3236 \cdot \rho^{-0.107} \tag{4}$$

where v the Poisson's ratio, ρ the density.

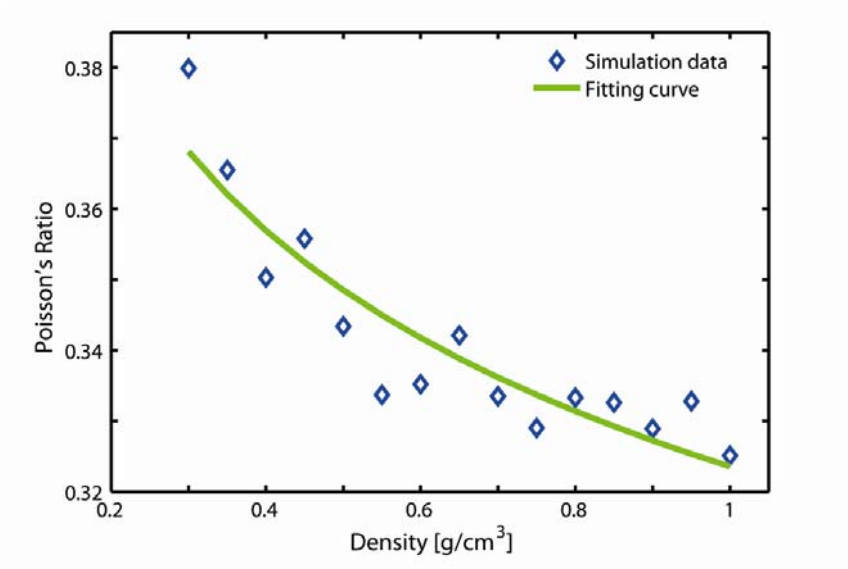

Fig. 3 The relation between Poisson's ratio and the density (The small diamonds refer to the simulation results. The green curve refers to the power-law fitting curve of simulation data.)

3.4 Constitutive relation

Considering the nanoscale pores of silica aerogels, we assume that silica aerogels are homogenous and isotropic materials, meaning that only two of the elastic coefficients, such as Young's modulus and Poisson's ratio, are sufficient to take all the elastic properties in. The constitutive relation of silica aerogels is same as elastic material and can be expressed as following.

$$\sigma_{ij} = C_{ijkl}\varepsilon_{kl} \tag{5}$$

where σ_{ij} the stress tensor, ε_{kl} the strain tensor, C_{ijkl} the forth-order tensor of elastic constant, which is expressed as following:

$$C_{ijkl} = \lambda\delta_{ij}\delta_{kl} + \mu(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) \tag{6}$$

where λ the Lame constant, μ the shear modulus,

$$\lambda = \frac{\nu E}{(1+\nu)(1-2\nu)} \quad , \quad \mu = \frac{E}{2(1+\nu)} \tag{7}$$

and

$$E = 9.638 \times 10^{-7} \cdot \rho^{3.378} \quad , \quad \nu = 0.3236 \cdot \rho^{-0.107} \tag{8}$$

4. Conclusion

Molecular dynamics simulations of silica aerogels with the density from 0.3g/cm^3 to 1.0g/cm^3 are carried out to investigate the mechanical properties. An improved method of generating the porous structures, which is derived from the negative pressure rupturing method, is proposed and it shows better stability while the density of silica aerogels is above 0.8g/cm^3. The Young's modulus and Poisson's ratio are obtained by uniaxial and biaxial tension tests respectively, and they both are found to be in a power-law relation to the density with the exponent of 3.378 and -0.107. Thus, assuming silica aerogels as homogenous and isotropic materials, the constitutive relation is the same as elastic materials which are determined solely by Young's modulus and Poisson's ratio.

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