ABSTRACT

Aerogels have been of interest to the aerospace community primarily for their thermal properties, notably their low thermal conductivities. While such gels are typically fragile, recent advances in the application of conformal polymer layers, as well as the development of computational models, allow for the performance of computer simulations of aerogel thermal conductivity and tensile and compressive failures, with results that are in qualitative, and sometimes quantitative, agreement with experiment. However, recent results in our laboratory suggest that gels having similar densities may exhibit substantially different properties. In this work, we extend our original diffusion-limited cluster aggregation (DLCA) model for gel structure to incorporate additional variations in simulation parameters, in the spirit of producing DLCA clusters of similar densities that nevertheless have different fractal dimension and secondary particle coordination. We perform particle statics simulations of gel strain on these clusters, and consider the effects of differing DLCA simulation conditions, and the resultant differences in fractal dimension and coordination, on gel strain properties.

INTRODUCTION

Silica aerogels are low-density materials whose thermal properties have been of ongoing interest for a wide variety of applications [1-3]. While pristine gels are fragile, polymer coating gels can greatly improve their strength while minimally impacting their insulating properties [4]. In order to provide a microscopic understanding of the mechanical behavior of the gels, and to provide a predictive tool of use in the further development of new aerogel technologies, we have performed molecular statics simulations of gel strain on a set of clusters with differing parameters, to observe the similarities and differences of silica aerogels. The model is based on computer simulations using a modified diffusion-limited cluster aggregation (DLCA) scheme to generate model gel structures, and combined atomic-scale static calculations whose results are abstracted into input for large-scale particle-scale failure simulations. In previous related work we have found our methodology produces qualitatively reasonable strain and failure behaviors, with the details of which depend on model gel density [5]. However, recent studies in our laboratory have found that aerogels having the same density may nonetheless exhibit substantially different thermal and mechanical properties [6]. Therefore we have initiated our early exploratory work in an attempt to determine whether varying the DLCA simulation parameters other than density can reproduce this observed behavior.

AEROGEL STRUCTURE

Aerogels exhibit a roppy, low-density morphology that displays three levels of structure. X-ray and neutron probes suggest that the gels consist of disordered aggregates of connected fractal clusters, with fractal behavior evident over a limited range of length scales [6-8]. Fractal dimensions of 1.7 to 1.8 at small length scales have been observed in low-density colloidal materials [9].

The smallest structural detail is the so-called "primary" particle, a few nanometers in diameter, consisting of approximately 50-150 amorphous silica. Primary particles are an order of magnitude larger, and typically somewhat lower in density. Secondary particles, in turn, are connected via interparticle bridges, and form the observed porous structure that may range from a "pearl-necklace" network, to a denser, more highly coordinated structure. It has been reported that gels having the same density may nonetheless exhibit differing properties.

STRUCTURAL MODEL

Our structural model consists only secondary particles, which are assumed to be homogenous; their detailed structure and any internal degrees of freedom are frozen. Primary particles are united, or are chosen at random from log-normal or truncated Gaussian distributions, with a mean radius of 15 nm.

Model gel structures are produced by DLCA computer simulation [10].

- 1000 single-particle clusters (secondary particles) are distributed at random without overlap in a computational box whose side determines the density. Cluster aggregation proceeds via repeated random walk/growth cycles.
- A cluster to be moved is chosen at random with probability P = 3[(1 - hi2)], where hi and m are the masses of the moving cluster, and the lightest cluster in the cell, respectively, and i is a scaling parameter.
- The moving cluster is given a small "driftless" displacement in a random direction. If no overlap occurs, the colliding clusters are merged into a single cluster with the point of collision.
- The simulation terminates when only a single cluster remains.

The following DLCA parameters are varied in an attempt to determine the sensitivity of fractal dimension, coordination, and strain energy on simulation conditions.

- Cluster diffuse step size (2, 3, 5, 7.5, and 15 nm)
- Particle size distribution method and width (uniform, log-normal, or truncated Gaussian distributions with widths of 3, 4.7, 7.10, and 15 nm)
- Probability scaling exponent (1.0, 0.25, 0.5, 0.75, and 1.0)

A default parameter set is defined, with stepsizes 1.0 nm, i = 0.7, and uniform particle sizes.

STRUCTURAL MODEL RESULTS—FRACAL DIMENSION

DLCA simulations were performed for a range of densities (0.0377 g/cm3, 0.0315 g/cm3, and 0.0220 g/cm3), designated low, medium, and high, respectively, and are representative of typical aerogel densities [11]. First-state representative low- and high-density colloidal particles are presented in figures 4(a) and 5(a).

ATOMIC SIMULATION OF BRIDGE STRAIN

We assume that interparticle interactions are described by a radii potential. The form of this potential is obtained from molecular statics simulations on an amorphous silica computational cell consisting of two representative spherical secondary particles connected by a bridge. In previous work, we have included an additional unfamiliar component in the potential with a radial component alone, failure is found to be too drastic. In the interest of computational efficiency, we have modified the angular force for the work, which is similar to the one used in our previous work.

Atomic interactions are described by a Rappe-Goddard potential [12], which consists of a short-range Morse component and a Coulomb component. Morse parameters are listed in table 1.

Table 1.—Rappe-Goddard potential parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>α</td>
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<tr>
<td>r0</td>
<td>0.0014</td>
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<tr>
<td>D</td>
<td>0.557</td>
</tr>
<tr>
<td>β</td>
<td>1.22e</td>
</tr>
<tr>
<td>r0</td>
<td>0.0014</td>
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</table>

Bridge strain results

A sequence of images from the bridge strain simulation are shown in figure 4, and bridge strain energy is shown in figure 5. While many phenomena indicate the straining and breaking of smaller substructures are evident, the energy curve generally appears to resemble the Universal Binding Energy Relation of Rose, Fermini and Smith [12], and, as such, can be fit to a Morse potential function. The function describes how the Morse function is in the atomic simulations in that it represents the sum of atomic-scale interactions between secondary particles; its range is much smaller relative to secondary particle size, than an atomic Morse potential, for example, as used in the bridge strain energy simulations.

CONCLUSIONS

We have performed computer simulations of the tensile strain and failure of silica aerogels, based on a multiscale model for cluster interactions, and a diffusion-limited cluster aggregation model for the gel structure. The simulations were carried out at an expanded density typically having core properties with respect to variation in simulation parameters. Over the range of parameters studied, only changes in density cause significant differences in cluster fractal dimension and energetics. Therefore we do not have a model that successfully explains differences in properties among clusters having the same density. It has been suggested that simple DLCA clusters form a universal long-range structure that is both fragile and that leads to an important structural feature of aerogels: the observed fractal nature. It is clear, however, that the additional variation in particle size that is included in the current model may be too. The degree of being to probe cluster failure properties and yield different strain energy distributions, and different strain behaviors.

REFERENCES


GEL CLUSTER STRAIN

Tensile strain is applied to DLCA clusters via a nanoscale particle state approach. A displacement of 0.1 mm is applied to a rigid slab at the top of the cluster, and the remaining particles in the cluster are then relaxed along the local energy gradient, and with the aim of producing DLCA clusters of similar densities that nevertheless have different mechanical behavior. Energy versus slab displacement is shown in figures 7(a) to (d). As with the fractal dimension, the density (α) is the dominant variable. Although the energy curves are quite noisy (additional runs, for the purpose of smoothing interparticle curves via averaging, are under way), a simple linear fit to the lower portion of each curve provides qualitative information. The highest-density cluster is the stiffest, with the other three showing only small differences. There is no meaningful variation in energy with stepsizes (β), α (β), and α (β), and α (β).

BRIDGE STRAIN RESULTS

Figure 4.—Sequence of bridge strain simulation.

Figure 5.—Energetics of interparticle bridge tensile strain.

Figure 6.—Initial and final states of strained DLCA clusters. (a) 0.0377 g/cm3, (b) 0.0315 g/cm3, (c) 0.0220 g/cm3.

Because we do not expect fracture behavior to be correct in detail due to the absence of the angular term, we instead concentrate on the small-strain energy dependence. Energy versus slab displacement is shown in figures 7(a) to (d). As with the fractal dimension, the density (α) is the dominant variable. Although the energy curves are quite noisy (additional runs, for the purpose of smoothing interparticle curves via averaging, are under way), a simple linear fit to the lower portion of each curve provides qualitative information. The highest-density cluster is the stiffest, with the other three showing only small differences. There is no meaningful variation in energy with stepsizes (β), α (β), and α (β), and α (β).