Molecular Dynamics Simulation on Self-Assembly of Nano-porous Structure of Polymer Cross-linked Silica Aerogels

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Abstract. The atomic structural model and mechanical properties of polymer cross-linked silica aerogels were simulated and calculated based on the molecular dynamics principles. The self-assembly process of network structure was studied, the solid skeleton of polymer cross-linked aerogels with different density were compared and analyzed, and the stress-strain relationships curves were figured out through application of strains on the cells. The self-assembly process shows that the polymer chains form a coating layer on the surface of the silica nanoparticles. The structural analysis indicates that all systems are amorphous structure and the solid skeleton is gradually thickened with increasing density. Elastic modulus rise from 85.39 to 213.94 MPa when densities increase from 0.236 to 0.521 g/cm^3.

1. Introduction

Aerogel is a kind of nano-porous structure material, with ultra-low density, high porosity, high specific surface area and low thermal conductivity, and can be widely used in the fields of building energy-saving, biomedicine, aerospace, adsorption catalytic, et al.[1].The network structure of silica aerogel contains primary and secondary particles, and the cross-linked secondary particles form irregular holes. The small contact area between secondary particles results in slippage and brittle fracture of silica aerogel under load[2,3]. The bonding strength of secondary particles can be improved by polymer modification, which is equivalent to form a “coating” on the surface of the secondary particles, thus enhancing the solid skeleton structure [4].

Molecular dynamics (MD) simulation can be used to calculate structure and property of aerogels. Kieffer and Angell et al[5] found that the fractal dimension and density of aerogels were linearly dependent. Bhattacharya and Kieffer[6] simulated the formation of porous skeleton of silica aerogel during sol-gel process. Rivas Murillo et al[7]studied the relationship between mechanical properties, fractal dimension and density of silica aerogel. Liu et al[8]established silica aerogel model by expansion and cooling, and the fractal dimension decreased with the decreasing of density. In this work, the self-assembly process of polymer cross-linked silica aerogels was simulated through the Forcite module of Materials Studio(MS), and the porous structure and mechanical properties of different systems were compared and analyzed based on MD theory.

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2. Model and calculation

2.1. The establishment of the N3300 polymer chain

Firstly, the ball stick model of tri-isocyanate Desmodur N3300 was established, and then energy was minimized by using geometry optimization.The optimized ball stick model of monomer is shown in Figure 1(b). Red, blue, gray, white balls are oxygen, nitrogen, carbon and hydrogen respectively. The N3300 monomers could be seed to produce dendritic molecular structures. Firstly, the nearest two N=C double bonds from different isocyanate groups broke, in which one lost its –C=O and the other one broke its double bonds between nitrogen and oxygen atoms, in order to form –NCO and –N sites, then the two remained sites linked together to form the new urea bond (-NH-C=O-NH-). Finally the polyurea chain through urea linkage was establish. The model of polymer chain with 736 molecules was optimized with smart method. figure 2(a) shows a fully linked amorphous polymer, in which one N3300 molecule is connected to three other Desmodur N3300 molecules.

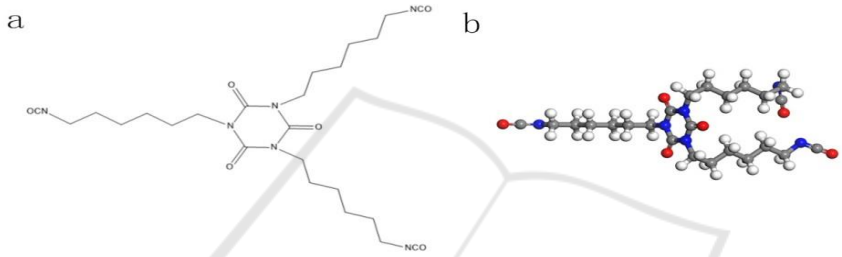


Figure 1. The model of tri-isocyanate Desmodur N3300: (a) molecular structure, (b) ball stick model.

2.2. The establishment of silica aerogel nanoparticles

Firstly, a 2×2×2 supercell was developed based on initial model and randomly broken bond. Here it follows a principle that the chains composed by silicon and oxygen atoms are connected with each other to form the three-dimensional reticular skeleton. Repeat processes above, and a density of 0.172 g/cm^3 aerogel particles was obtained. Finally, hydrogen was added to simulate the real structure of aerogel nanoparticles. The optimized aerogel nanoparticle is shown in figure 2(b).

2.3. The establishment of polymer cross-linked aerogel

Silica aerogel nanoparticles and N3300 polymer chains accounted for 35.1% and 64.9% respectively were assembled by the amorphous cell module. The density of cell was set to 0.450 g/cm^3 and the length was 57.284 Å .The precision of calculation was set as fine and the compass field was selected. The optimized composite model is shown in figure 2 (c).

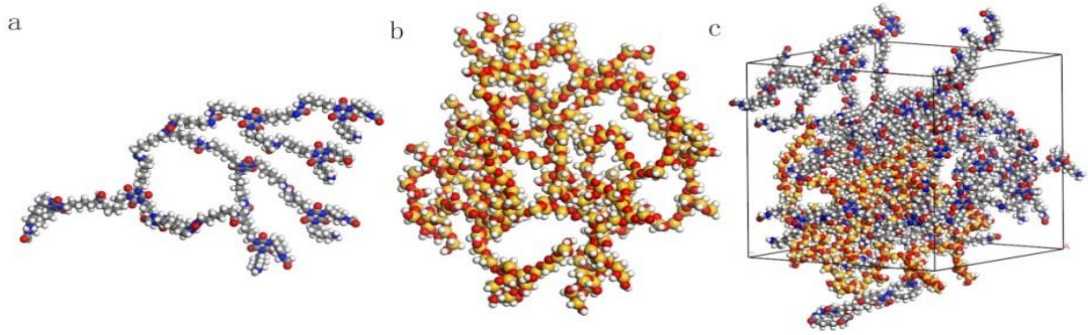


Figure 2. Structure models: (a) N3300 polymer, (b) the nanoparticle of silica aerogel and (c)the cell of composite aerogel

2.4. Dynamic calculation

Supercell containing 53296 atoms was established, and the length of system was 114.569 Å. Firstly, NVT ensemble was selected, Nosé-Hoover thermostats were used to control the temperatures (3000 K) in the canonical. Then Atom based was selected to calculate the Vander Waals interactions and electrostatic interactions. The execution time was 200 ps, with the time step of 0.1 fs. Finally the polymer cross-linked aerogel was calculated to equilibrium state.The temperature and energy change of the system at 3000 K are shown in figure 3 and 4. It can be seen that the fluctuations of temperature and energy were significantly reduced after 15 ps, which indicate that the simulation system has been fully balanced.

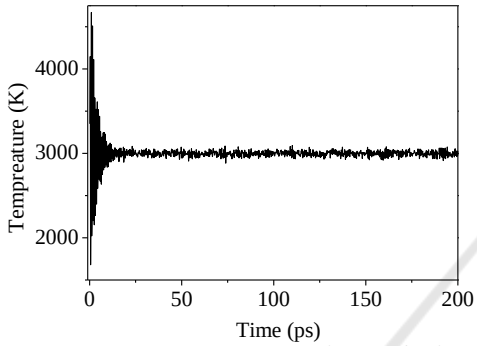


Figure 3. Temperature vs. time of simulation system

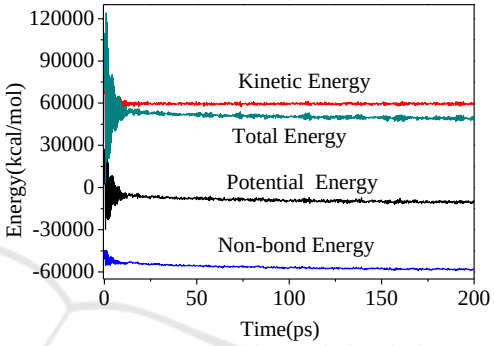


Figure4. Energy vs. time of simulation system

The models of polymer cross-linked aerogels with different density are shown in figure 5. It can be shown that the polymer chains filled the pores of the nanoparticles and interlinked with each other to form network skeleton.

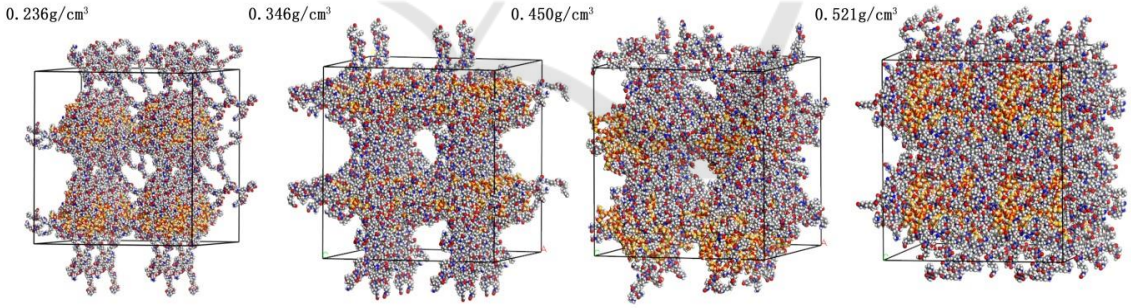


Figure 5 . Structural model of polymer cross-linked aerogels at four different densities

A partial enlargement of the composite aerogel model is shown in figure 6 As can be seen that the polymer chains were concentrated on the surface of the skeleton, which was equivalent to increase the contact area between secondary particles and thicken the three-dimensional solid network.

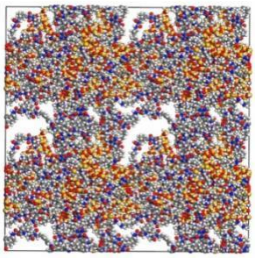


Figure 6.Partially enlarged view of the structure of composite aerogel

3. Results and analysis

3.1. The Analysis of Model Conformational

The structural model of aerogel (0.450 g/cm^3) in different moments are shown in figure 7 The polymer chains and nanoparticles were relatively uniform distributed throughout the cell in the initial model. During 50 ps and 100 ps, the polymer began to approach the nanoparticles and formed a dense polymer shell covering the surface of the skeleton. At 150 ps, the pores gradually expanded through the entire framework structure. At 200 ps , the polymer chains formed a coating layer on the surface of the nanoparticles ,and the clusters got closer.

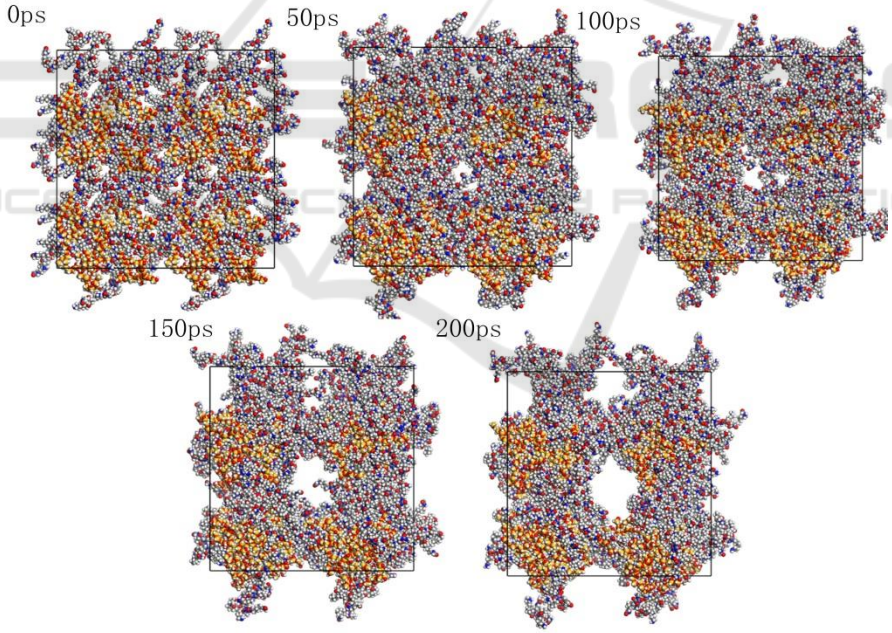


Figure 7.Structure models of 0.450g/cm^3 composite aerogels at different time

3.2. The structural analysis

The radial distribution function (RDF) gives a measure of the probability that, given the presence of an atom at the origin of an arbitrary reference frame, there will be an atom with its center located in a spherical shell of infinitesimal thickness at a distance , r , from the reference atom. It can be used to determine the short range order of the simulated system. The RDF of polymer cross-linked aerogel with different density are shown in figure 8. It can be seen that the structural characteristics

of short-range order and the long-range disorder, which proves that all the models are amorphous structures. The intensity of peak increases with the increasing density, indicating that the force between atoms gradually increases.

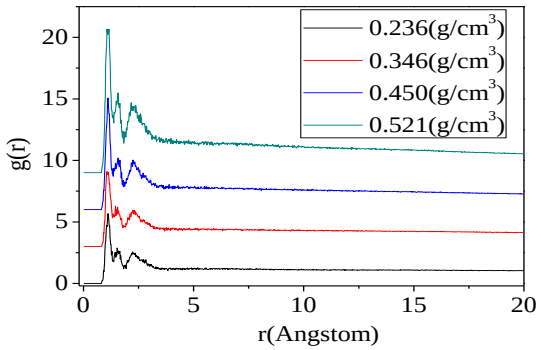


Figure 8. Radial distribution function of different systems

The isosurface and density field distributions of cross-linked polymer aerogel with different densities are shown in table 1 From left to right, it represents the isosurface, isosurface slices, density distribution of carbon element and density field slices, respectively. It can be seen that red, yellow, blue and gray regions represents the distribution of oxygen, silicon, nitrogen and carbon respectively. The middle cross-linked areas of red and yellow represents SiO_2 aerogel particles. The connected areas of blue and gray represents polymer chains. The isosurface distribution was irregular and formed continuous mesoporous aerogel morphology when the density was within this range.

In the density distribution figure of different models, red region represents the density of 0 g/cm^3, and the blue region represents the highest density. The network structure of isosurface corresponds to the cross-linked areas of blue and green in the density field, which indicates that the carbon elements are concentrated in this area. The nanopores of isosurface corresponds to the red areas in the density field. Therefore, the internal skeleton structure can be further observed through inner slices. Comparing the different isosurface, It can be seen that the polymer chains were randomly distributed within the framework of silicon skeleton. Comparing the density field slices of carbon elements, it can be seen that carbon element distribution was relatively uniform and formed the connected areas with different shapes when the density was 0.236 g/cm^3, which proved that the solid network skeleton has been formed. The solid skeleton gradually becomed thicker and the size of nano-meter holes decreased gradually with increasing density.

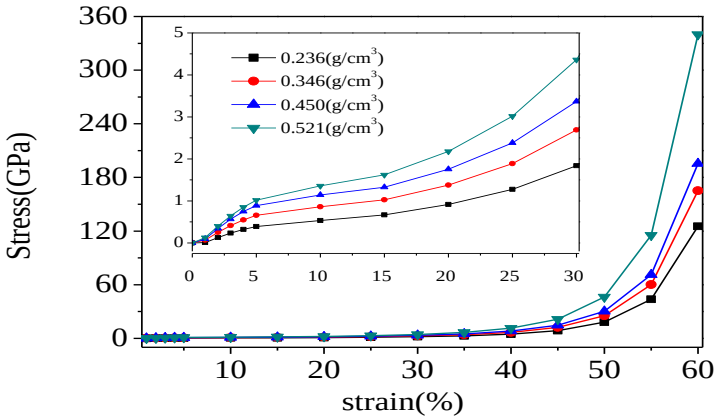


Figure 9. Stress-strain curve of composite aerogel with different densities during compression.

3.3. The analysis of mechanical properties

Figure 9 shows the stress-strain curve of composite aerogel with different density in uniaxial compression. There are three characteristic stages: elastic, compacted and dense. The structure showed elastic deformation when the strain was 0-5%, the pore walls appeared different deformation and the holes shrank with different degrees under external force[9].The pores began to collapse and the structure was destroyed when the strain was 5% -15%. The stress increased sharply with the increasing of strain when the strain exceed 15%, and the skeleton structure further contacted with each other when the strain was continually imposed.

The slope of 0~5% in the curve represents aerogel's elastic modulus, the elastic modulus of different models is shown in table 2.

Table 1. The isosurface and density field distribution of equilibrated structures.

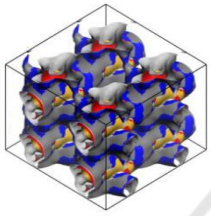
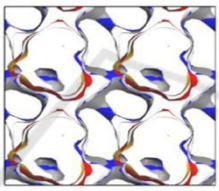
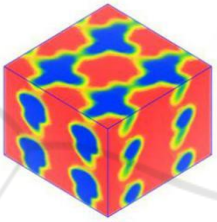
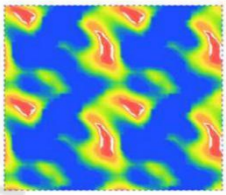
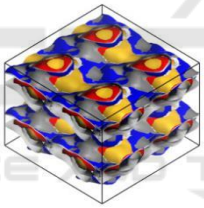
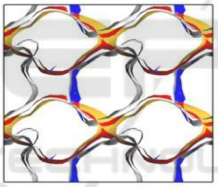
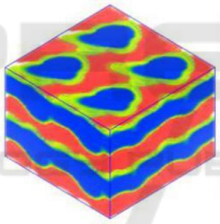
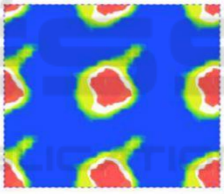
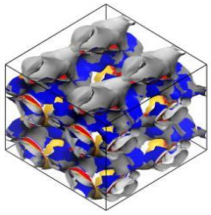
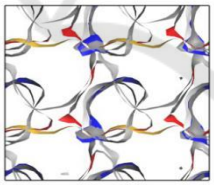
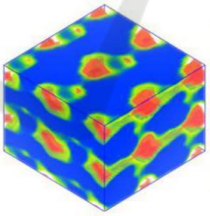
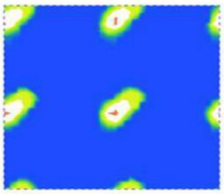
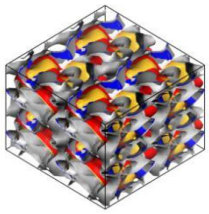
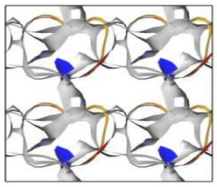
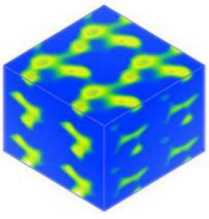
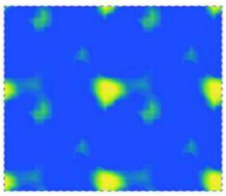
Density (g/cm^3)	isosurface	isosurface slices	density distribution of carbon element	density field slices of carbon element
0.236				
0.346				
0.450				
0.521				

Table 2. Elastic modulus of composite aerogels with different densities.

Density (g/cm^3)	0.236	0.346	0.450	0.521
Elasticmodulus (MPa)	85.39	139.50	189.75	213.94

The calculated values are in the same order of magnitude as the experimental values. Yan et al.[10] preparaed high strength composite silica aerogel which have a compressive modulus of 82.37 MPa. Tang et al.[11] used disocyanate modification, and the high strength modified aerogels with elastic modulus of 116.7MPa were obtained. Katti et al.[12] added an isocyanate in SiO_2 sol ,and aerogel achieved the elastic modulus of 129 ± 8 MPa.

4. Conclusions

The atomic scale model of polymer cross-linked aerogel was constructed by molecular dynamics, and the process of atomic self-assembly was simulated. The polymer chains coat on the surface of nanoparticles, and link with each others to form the reticular skeleton structure.

All equilibrated systems are amorphous structures.The solid skeletons gradually become thicker and the size of nanometer holes decrease with increasing density. The simulation results of mechanical properties and experimental values are in the same order of magnitude. The elastic modulus increase from 85.39 to 213.94MPa as density changes from 0.236 to 0.521 g/cm^3.

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