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Geometric and finite element modeling of biopolymer aerogels to characterize their microstructural and mechanical properties

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Biopolymer aerogels belong to a class of highly open-porous cellular materials. Their macroscopic mechanical properties (such as elasticity or thermal conductivity) depend on microstructural features (namely pore size distribution (PSD), fiber diameter and solid fraction), which can be tailored by different synthesis and drying routes. The design of modern aerogel materials requires a better perception into the microstructure and its influence on the mechanical properties. To predict the material properties using simulation, it is significant to construct a geometric model which is sufficiently precise to represent the microstructure of real materials. A tessellation approach based on Voronoi diagrams is a powerful tool to model such cellular-like materials. In this contribution, the diversified cellular morphology of aerogels is described computationally using a Voronoi tessellation-based approach [1]. Accordingly, Voronoi tessellations are generated to create periodic representative volume elements (RVEs) resembling the microstructural properties of the cellular network. Stress-strain curves resulting from finite element simulations of these RVEs and experiments of the aerogels under compression are compared. This work is an extension of our previous Voronoi tessellation-based on the 2-d description of biopolymer aerogels [2].

1 Introduction

Aerogels belong to a special class of nanoporous cellular materials characterized by unique physical properties, such as a low bulk density and low thermal conductivity. Recently, biopolymer aerogels have gained more attention due to their sustainability, ease of functionalization and tunable properties. Due to the biocompatible and biodegradable properties of biopolymer aerogels, they are intensively used as drug carriers in the biomedical industry and for food packaging in food industry [3]. The current rise in applications demands to study the mechanical properties of biopolymer aerogels. In general, biopolymer aerogels are characterized by a cellular-like appearance exhibiting an irregular microstructure with random pore sizes and shapes. The mechanical properties of such aerogels are highly influenced by their microstructural features (namely pore size distribution (PSD), fiber diameter and solid fraction). Computational modeling, including geometric design and FE simulation, is a cost- and resource- efficient technique to study such structure-property relations. To this end, fully periodic representative volume elements (RVEs) representing the realistic 3-d pore morphologies of biopolymer aerogels are developed using the Laguerre-Voronoi tesselation (LVT) based on random closed packing of polydisperse spheres (RCPPS). These RVEs are then simulated under compressive loading using finite element method (FEM) to investigate their mechanical properties.

2 Methods

The microstructure of aerogels is modeled using LVT based on RCPPS, where the spatial configuration of spheres obtained from RCPPS is used to construct the Voronoi diagram in Laguerre geometry [4]. First, the RCPPS is obtained such that the volume distribution of the packed spheres adheres to the experimentally obtained PSD of κ-carrageenan aerogels. Consequently, the LVT is carried out for the point set consisting of sphere centers and the corresponding radii obtained from RCPPS. Accordingly, the RCPPS serves as an input template for LVT in constructing the microstructure of aerogels. In order to fit the cell volume distribution of resulting Voronoi diagram to the experimentally obtained PSD, centroidal LVT is carried out based on a generalized Lloyd algorithm with volume constraints [5].

2.1 Finite element (FE) modeling

The resulting Voronoi diagram is reconstructed to a cube-shaped RVE with periodic boundary nodes (Fig. 1a). The cell edges of the Voronoi structure represent the cell wall fibers in the aerogel network. Hence, these edges are imported as line bodies and meshed as FE beam elements with circular cross-section in LS-DYNA. The fiber diameters were calculated theoretically by preserving the experimentally obtained structural properties (PSDs and solid fraction). The Hughes-Liu beam element formulation with cross-section integration is used. A linear elastic material model with a Young's modulus of 4.5 GPa is assigned to the beam elements [6]. An automatic general contact algorithm (*CONTACT_AUTOMATIC_GENERAL) in LS-DYNA is used to model the beam-to-beam contact, in order to avoid the penetration between the fiber walls (i.e. beam elements)

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during deformation. An RVE in combination with periodic boundary conditions (PBCs) has the potential to obtain the homogenized macroscopic response. The motion of boundary node pairs is constrained to each other using PBCs, such that the stress continuity across the boundaries is preserved during deformation. The displacement and rotational degrees of freedom of the periodic boundary node pairs are constrained to a dummy node using *CONSTRAINED_MULTIPLE_GLOBAL and *CONSTRAINED_LINEAR_GLOBAL keywords respectively in LS-DYNA. A detailed procedure on FE modeling is discussed in [4].

3 Results

The stress-strain responses of the resulting FE models corresponding to 1 & 3 wt.% κ-carrageenan aerogels show good agreement with the corresponding experimental curves when subjected to uniaxial compression (Fig. 1b). In cellular materials, the dependency of the macroscopic Young's modulus (E) on the envelope density (ρ_e) is studied using the scaling law $E/E_s \propto (\rho_e/\rho_s)^\alpha$, where E_s and ρ_s are the Young's modulus and density of the solid skeleton [7]. In our investigation [4], the exponent $\alpha = 1.76$ is obtained from the simulation. The model shows isotropic behavior when subjected to uniaxial compression in all three mutually orthogonal directions.

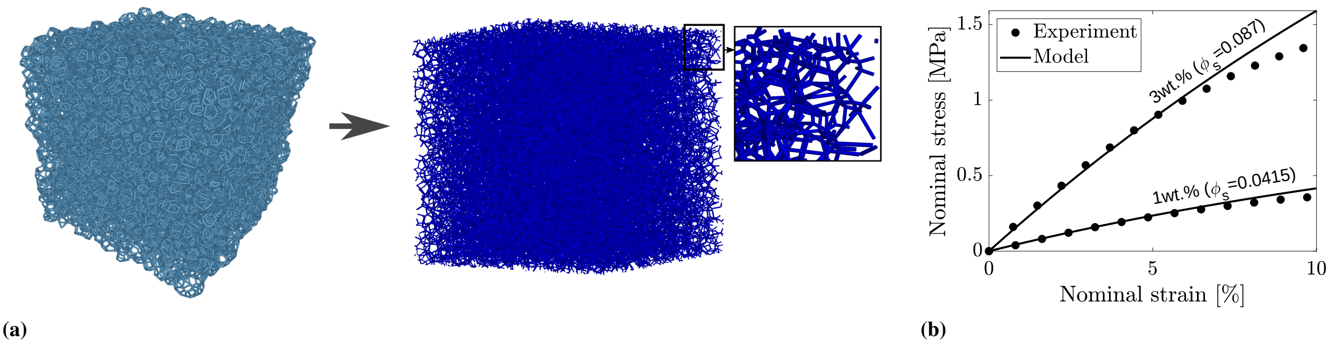

Fig. 1: (a) Reconstruction of LVT (left) to cube-shaped RVE (right) corresponding to 1wt.% κ-carrageenan aerogel, (b) bulk mechanical behavior of 1 & 3 wt.% κ-carrageenan aerogels.

4 Conclusion and outlook

The FE model inheriting the PSD of real aerogel is capable of predicting their macroscopic mechanical behavior. The model captures the compressive response of the bulk material as a consequence of local bending and buckling of cell walls. The softening of stress-strain response at higher compressive strain can be obtained by incorporating damage-based material model. The PSD, solid fraction and fiber properties are experimentally obtained parameters so that the proposed modeling approach does not require parameter identification through curve fitting. Note that the proposed procedure is not only limited to aerogels and can be optimized also for other open-porous cellular materials.

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References

[1] G. Voronoi, Journal für die reine und angewandte Mathematik **134**, 198-287 (1908).
[2] A. Rege, M. Hillgärtner and M. Itskov, The Journal of Supercritical Fluids **151**, 24-29 (2019).
[3] S. Zhao, W. J. Malfait, N. Guerrero-Alburquerque, M. M. Koebel and G. Nyström, Angewandte Chemie International Edition **57**, 7580-7608 (2018).
[4] R. Chandrasekaran, M. Hillgärtner, K. Ganesan, B. Milow, M. Itskov and A. Rege, Scientific Reports **11**, 10198 (2021).
[5] D. P. Bourne, P. J. J. Kok, S. M. Roper and W. D. T. Spanjer, Philosophical Magazine **100(21)**, 2677-2707 (2020).
[6] A. J. Granero, J. M. Razal, and G. G. Wallace, Journal of Materials Chemistry **20(37)**, 7953-7956 (2010).
[7] A. P. Roberts and Edward J. Garboczi, Journal of the Mechanics and Physics of Solids **50(1)**, 33-55 (2002).

