Stiffening of biopolymer aerogel networks upon wetting: a model-based study

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Abstract

The mechanism behind the stiffening effect observed in the stress-strain response of alginate-starch aerogels upon being exposed to wetting is investigated in this paper, via a physically motivated model approach. A network decomposition concept is introduced, whereby the highly nanoporous network is decomposed into a swollen aerogel network and a hydrogel-like network. The aerogel network is modeled by considering idealized square-shaped microcells of varying sizes. An attempt is made to explain the stiffening of the network, upon wetting, based on changes in the fibril characteristics of the aerogel network upon swelling and formation of a hydrogel-like phase in the microporous region. In this first approach, the aerogel network is described based on a micro-mechanical model, while the hydrogel-like network is described using a phenomenological one. The results of the proposed model idea are in very good agreement with the experimental data of alginate-starch aerogels under different degrees of wetting.

Keywords: biopolymer, wetting, aerogel, hydrogel, model

1. Introduction

Biopolymer aerogels exhibit a highly nanoporous network formed of interconnecting fibrils, giving their morphology a cellular appearance [1]. Such aerogels, polysaccharide-based in particular, have received tremendous boost in academic research as well as industrial biomedical applications in recent years [1, 2]. Of special interest are their mechanical properties and behavior, since these are crucial in considering such materials for tissue engineering applications, as for e.g., scaffolds [3, 4]. While there have been studies reporting on the mechanical behavior of such polysaccharide-based aerogels, papers elucidating the effect of swelling on the mechanical properties of aerogels are relatively scarce.

Biopolymers are often intrinsically hydrophilic and thus can uptake water both from vapor as well as liquid phase. It has been observed experimentally that there is a critical water content above which the porous aerogel network undergoes a partial irreversible collapse [5, 6]. The reason is well known in the drying theory and lies in the fact that the co-existence of liquid water and water vapor in a single pore results in substantial capillary forces and thus macroscopically observed collapse. Similarly, a gradual water uptake from the vapor phase leads to shrinkage in a degree proportional to water concentration, i.e. relative humidity [7]. Importantly, there is also a critical relative humidity below which the shrinkage is almost negligible and water desorption is fully reversible. Below a certain degree of wetting the aerogel network can resist capillary forces. We suggest that the following scheme of water uptake applies to biopolymeric aerogels: At storage of an aerogel in a humid air, all fibrils absorb water, independent if they bound a large pore or a micropore. Once their capacity of water uptake is reached, the micropores first fill with water and establish a microporous hydrogel-like phase in the network. At higher water partial pressures the mesopores fill and at latest the macropores being in the range of a micrometer. We suggest therefore, that the mechanical behavior of biopolymeric aerogels exposed to humidity can then be modelled with different set-ups, depending on the amount of water absorbed.

The mechanical behavior and properties of cellular biopolymer aerogels have been modelled based on the microcell approach first proposed in Rege et al. [8]. The model idea was based on the assumption that the aerogel network is formed of idealised square-shaped microcells with varying fibril lengths, which were determined with the help of the pore-size distributions obtained via the nitrogen desorption isotherms that were imported into the Barrett-Joyner-Halenda (BJH) model [9]. The macroscopic mechanical deformation is dictated by the kinematics of the microscopic cell wall fibrils. Accordingly, the non-linear Euler-Bernoulli beam theory was used to describe the nature of the fibril under very large deflections. The collapse of microcells was based on the bending stress in the fibrils reaching a critical value. The overall macroscopic predictions of the model were in good agreements with the uniaxial compression data of cellulose, pectin and k-carrageenan aerogels [10].

In this work, the model is extended to capture the stiffening in the aerogel network upon wetting. Recent study of alginate-starch aerogels subjected to wetting showed pronounced stiffening with increasing degree of wetting [7]. The aerogel spec-

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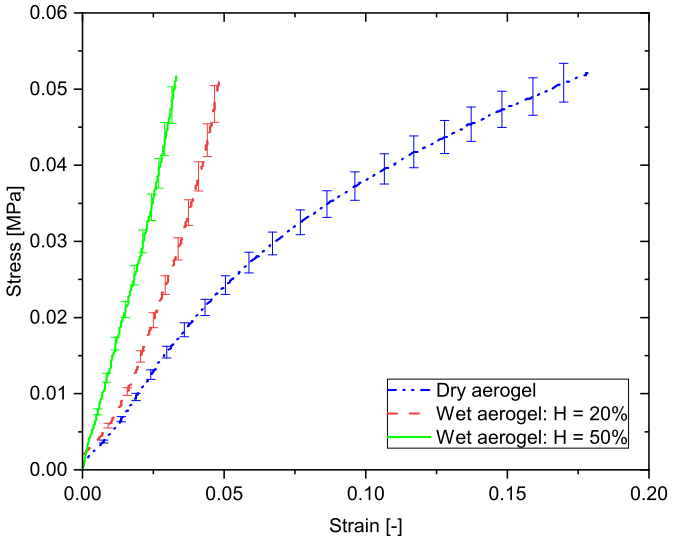

Figure 1: Experimental stress-strain curves from dry and wet alginate-starch aerogels. Error bars correspond to the observed relative difference between the largest and smallest values of the nominal stress across all aerogel samples.

imens were exposed to different degrees of relative humidity. The resulting experimental stress-strain curves are illustrated in Figure 1. Here, H is the amount of relative air humidity. Capillary effect starts playing a role here, with the water affecting the smaller pores first as explained above. This may result in the collapse of micropores due to swelling of fibrils and strong capillary forces. This could further explain the macroscopic shrinking of the aerogel specimen upon wetting. These collapsed pores form a hydrogel-like network. On the other hand, all the larger pores (mesopores and macropores) undergo swelling of their cell wall fibrils. This affects the fibrils in two ways: swelling increases their diameter, while their Young's modulus decreases [4].

The paper is organized as follows. The model setup and the concerned equations are described in Section 2. The model results are displayed along with their validation to the experimental aerogel stress-strain curves in Section 3. The conclusions and a brief outlook are presented in the last section.

2. Model setup

Both, the hydrogel-like network as well as the aerogel network contribute substantially to the mechanical behavior of the macroscopic aerogel. To mathematically elucidate this effect, a network decomposition concept is introduced. Hereby, the wet aerogel network is decomposed into a hydrogel-like network and a swollen aerogel network. The total network strain energy can be expressed in the following additive form:

$$\Psi = \Psi_{\mathrm{A}} + \Psi_{\mathrm{H}}, \tag{1}$$

where Ψ_A and Ψ_H denote the contribution of the swollen aerogel and the hydrogel-like network, respectively. The concept of this network decomposition is illustrated in Figure 2. The pore-size distribution is plotted as a function of the relative pore-area.

In this way, the amount of the aerogel network affected by wetting can be represented. The boundary of network decomposition is directly correlated to the degree of wetting H. So a 20% degree of wetting is considered to be represented by 20% of the network pore area being transformed into a hydrogel-like network while the remaining area remains as an aerogel network with swollen fibrils.

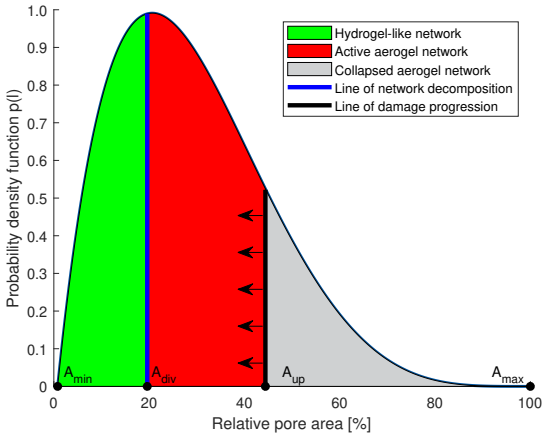

Figure 2: Illustration of the network decomposition concept. The grey region represents the hydrogel-like phase, while the orange plus blue region identifies the aerogel network. The blue region along with the line of damage progression shows that the microcells start collapsing from the larger to smaller ones.

The strain energy function for a single unit microcell within the aerogel network is defined by [10],

$$\psi_{\mathrm{A}} = \frac{2EI}{l}\left[a_1(1-\lambda)^4 - a_2(1-\lambda)^3 + a_3(1-\lambda)^2\right], \tag{2}$$

where, a_1, a_2, a_3 are geometric constants. Furthermore, E, I and l denote the Young's modulus, area moment of inertia and the length of the cell wall fibril, respectively. λ specifies the applied micro-stretch to a microcell. Note that the diameter of the cell wall fibrils increases with increasing degree of wetting, due to higher water absorption. Furthermore, the Young's modulus is lowered in the swollen network according to results reported by Quraishi et al. [4]. The damage in the aerogel network is dictated by the buckling of the cell wall fibrils. When the axial component of the force in the cell wall fibril reaches the critical buckling load, the fibril is considered to collapse. This criterion results in the failure of larger microcells through the network before the smaller ones. This is in agreement with the recent experimental observations that the larger pores collapse first. Using the procedure explained in Rege et al. [10], the total aerogel network response can be formulated as,

$$\Psi_{\mathrm{A}} = \sum_{i=1}^{k} \omega_i \int_{l_{div}}^{l_{up}(\lambda^{\boldsymbol{d}_i})} N_0\; p(l)\; \psi_{\mathrm{A}}(l, \lambda^{\boldsymbol{d}_i}) dl, \tag{3}$$

where N_0 denotes the total number of microcells in the network, $p(l)$ represents the probability density function based on the generalized beta one to describe the cell-size distribution. The limits l_{div} and l_{up} correspond to the limits shown in the Figure 2 and enclose only the active microcells in the aerogel network.

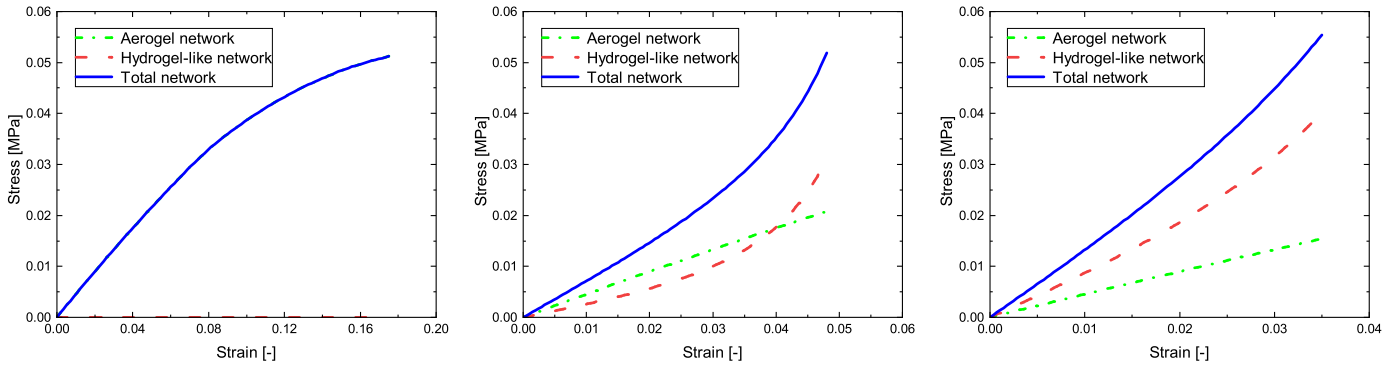

Figure 3: Demonstration of the contribution of aerogel and hydrogel-like network towards the constitutive response of the network. a) dry aerogel, b) 20% wet aerogel, c) 50% wet aerogel.

The concept of directional averaging over a unit microsphere is used, wherein the three-dimensional network response is obtained as a summation of the directional energies [11]. The ω_i specifies the weight factors used in the microsphere model and are numerically identified by using the algorithm proposed by Heo and Xu [12] using $k = 45$ directions.

The microporous hydrogel-like network is considered to be nearly incompressible. The mechanical behavior of hydrogels shows in general J-type stress behavior [13], which is similar to a hyperelastic material. This is a common observation and assumption in modelling the hyperelastic behavior of hydrogels [14]. Therefore, in the present work, hyperelastic models can be used as a tool to describe the behavior of microporous hydrogel-like network. In the literature, numerous such models have been proposed, such as the well-known Neo-Hookean model [15], Gent model [16] or the Ogden model [17]. By means of physical interpretation, these models utilize a phenomenological approach. Among these, the Gent model provides good interpretation of the nonlinear constitutive behavior of hydrogels. Unlike other models, the nonlinearity is also predicted under small deformations. The strain energy function for the Gent model is given by [16],

$$\Psi_{\mathrm{H}} = -\frac{\mu I_m}{2} \ln\left(1 - \frac{I_1 - 3}{I_m}\right), \tag{4}$$

where μ denotes the shear modulus and I_1 and I_m represent the first invariant of the right Cauchy-Green tensor $\mathbf{C}$ and the maximal value of I_1, respectively. Use of this energy function furthermore introduces only two additional new parameters, μ and I_m. This energy function applies to the hydrogel-like network in the microporous regime.

The network evolution is also illustrated in Figure 2. The hydrogel-like network is considered to be elastic within the small-deformation regime [18]. On the other hand, the aerogel-like network undergoes damage even in this regime, due to the buckling of larger fibrils. The contribution of the collapsed microcells within the aerogel network is not accounted in the evolving strain energy of the whole network. These collapsed cells contribute towards the densification of the network only under large deformations. The contribution of both the network strain energies is then used to formulate the constitutive equation in the form of the first Piola-Kirchhoff stress (nominal stress) versus the applied macroscopic stretch. It is necessary to note that an affine concept, as considered in our previous work [8], is used, which considers the microscopic stretches to follow the macroscopic deformation gradient.

3. Results and Discussion

The proposed model consists of seven parameters, apart from the two distribution ones (see Table 1). Of these, five physically motivated ones belong to the aerogel network model, while the other two phenomenological parameters belong to the hydrogel-like network model. The model response can then be obtained by pre-defining A_{div}, as discussed earlier.

Material parameter	Description
Aerogel network	
l_{min}, l_{max}	minimum and maximum length of fibrils
E	Young's modulus of fibrils
d_F	diameter of fibrils
N_0	initial number of microcells in the network
Hydrogel-like network	
μ	shear modulus
I_m	maximal value of I_1

Table 1: List of model parameters along with their description.

Figure 3 illustrates the contributions of the aerogel as well as the hydrogel-like networks towards the total network response. Figure 3a shows the dry aerogel behavior where the contribution of the hydrogel-like network is zero, as well as there are no swollen fibrils. Figure 3b demonstrates the influence of the hydrogel-like network on the total network response, by defining $A_{div} = 20\%$ of the total pore area of the network. This then corresponds to a 20% degree of wetting as seen in [7]. This influence is seen to be much more dominant in the 50% wetting curve as shown in Figure 3c. Finally, the proposed model results are validated against the experimental uniaxial quasi-static compression data of alginate-starch aerogels in Figure 4. The overall agreement of the proposed model is rather good. Since the only parameter to be fit to experimental data in the aerogel network model is N_0, and since it scales with the factor of the

increment of the density, the uncertainties in the model predictions are based on the uncertainties in the calculation of the densities of aerogels. The available experimental data of the wet aerogels [7] was limited to the small deformation regime due to the load-cell restrictions of the testing device. Future investigations would be focused on the performance of wet aerogels under larger compressive forces and thus under large deformation. But, within the moderate deformation regime, an extension to the model [10] by considering the network decomposition concept consisting of the swollen aerogel network and the addition of a hydrogel-like network seems to give good qualitative as well as quantitative predictions of the stiffening behavior due to wetting in alginate-starch aerogels thus tending towards a proof of concept of the model idea. More investigations into the microporous regime are necessary to reveal the microstructural changes towards the hydrogel formation. These are indispensable to propose a physically motivated hydrogel-like network strain energy. However, as a first approach, using the Gent strain energy function to describe the hydrogel-like network within the small deformation regime seems plausible.

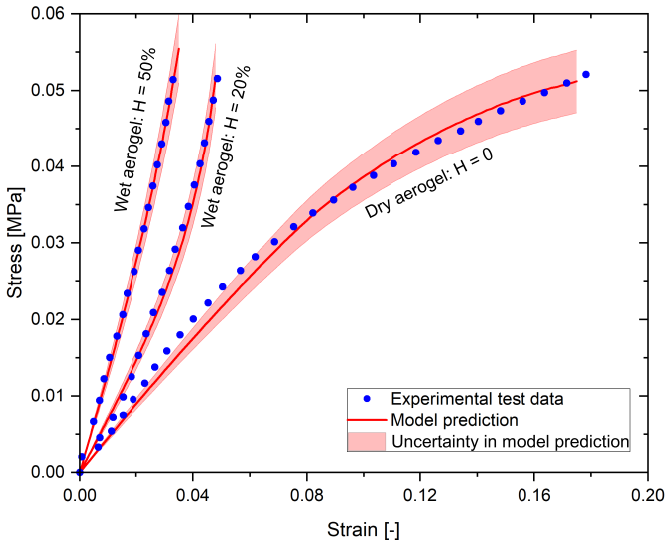

Figure 4: Model results versus the averaged experimental data of alginate-starch aerogels under compression (for error bars in the experimental data, refer to Figure 1), subjected to different degrees of wetting.

4. Conclusions

In conclusion, the proposed model approach attempts to describe the effect of wetting on the mechanical behavior of biopolymer aerogels. The observed stiffening in the network is attributed to the changes in the fibril characteristics due to swelling and the formation of a hydrogel-like network. This is modeled by introducing a network decomposition concept, where the aerogel network is described based on the model by Rege et al. [10], while the hydrogel-like network is described using the Gent model [16]. For further investigations, the wet aerogels need to be subjected to larger deformations to study the trends of the resulting stress-strain curves. Moreover, a physically motivated description of the hydrogel-like network is necessary to account for its microstructural effects and damage. For such a description, experimental characterization of this phase is imperative.

References

[1] S. Zhao, W. J. Malfait, N. Guerrero-Alburquerque, M. M. Koebel, G. Nyström, Biopolymer aerogels and foams: Chemistry, properties, and applications, Angewandte Chemie International Edition 57 (2018) 7850–7608.

[2] I. Smirnova, P. Gurikov, Aerogel production: Current status, research directions, and future opportunities, The Journal of Supercritical Fluids 134 (2018) 228–233. doi:10.1016/j.supflu.2017.12.037.

[3] M. Martins, A. A. Barros, S. Quraishi, P. Gurikov, S. Raman, I. Smirnova, A. R. C. Duarte, R. L. Reis, Preparation of macroporous alginate-based aerogels for biomedical applications, The Journal of Supercritical Fluids 106 (2015) 152–159.

[4] S. Quraishi, M. Martins, A. A. Barros, P. Gurikov, S. Raman, I. Smirnova, A. R. C. Duarte, R. L. Reis, Novel non-cytotoxic alginate-lignin hybrid aerogels as scaffolds for tissue engineering, The Journal of Supercritical Fluids 105 (2015) 1–8.

[5] P. Gurikov, S. P. Raman, D. Weinrich, M. Fricke, I. Smirnova, A novel approach to alginate aerogels: carbon dioxide induced gelation, RSC Advances 5 (2015) 7812–7818.

[6] R. Subrahmanyam, P. Gurikov, P. Dieringer, M. Sun, I. Smirnova, On the road to biopolymer aerogels-dealing with the solvent, Gels 1 (2) (2015) 291–313.

[7] S. Antonyuk, S. Heinrich, P. Gurikov, S. Raman, I. Smirnova, Influence of coating and wetting on the mechanical behaviour of highly porous cylindrical aerogel particles, Powder technology 285 (2015) 34–43.

[8] A. Rege, M. Schestakow, I. Karadagli, L. Ratke, M. Itskov, Micromechanical modelling of cellulose aerogels from molten salt hydrates, Soft Matter 12 (34) (2016) 7079–7088.

[9] E. P. Barrett, L. G. Joyner, P. P. Halenda, The determination of pore volume and area distributions in porous substances. i. computations from nitrogen isotherms, Journal of the American Chemical society 73 (1) (1951) 373–380.

[10] A. Rege, I. Preibisch, M. Schestakow, K. Ganesan, P. Gurikov, B. Milow, I. Smirnova, M. Itskov, Correlating synthesis parameters to morphological entities: Predictive modeling of biopolymer aerogels, Materials 11 (9) (2018) 1670.

[11] C. Miehe, S. Göktepe, F. Lulei, A micro-macro approach to rubber-like materials—part i: the non-affine micro-sphere model of rubber elasticity, Journal of the Mechanics and Physics of Solids 52 (11) (2004) 2617–2660.

[12] S. Heo, Y. Xu, Constructing fully symmetric cubature formulae for the sphere, Mathematics of computation 70 (233) (2001) 269–279.

[13] J. P. Gong, Y. Katsuyama, T. Kurokawa, Y. Osada, Double-network hydrogels with extremely high mechanical strength, Advanced materials 15 (14) (2003) 1155–1158.

[14] R. E. Webber, C. Creton, H. R. Brown, J. P. Gong, Large strain hysteresis and mullins effect of tough double-network hydrogels, Macromolecules 40 (8) (2007) 2919–2927.

[15] R. Rivlin, Large elastic deformations of isotropic materials iv. further developments of the general theory, Philosophical Transactions of the Royal Society of London. Series A, Mathematical and Physical Sciences 241 (835) (1948) 379–397.

[16] A. Gent, A new constitutive relation for rubber, Rubber Chemistry Technology 69 (1) (1996) 59–61.

[17] R. W. Ogden, Large deformation isotropic elasticity–on the correlation of theory and experiment for incompressible rubberlike solids, Proceedings of the Royal Society of London. A. Mathematical and Physical Sciences 326 (1567) (1972) 565–584.

[18] J. Hatton, G. R. Davis, A.-H. I. Mourad, N. Cherupurakal, R. G. Hill, S. Mohsin, Fabrication of porous bone scaffolds using alginate and bioactive glass, Journal of functional biomaterials 10 (1) (2019) 15.