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Perspectives in the modeling of biopolymer aerogel networks subject to wetting

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Alginate-based aerogels were shown to be non-cytotoxic and to feature good cell adhesion, thus drawing their attention towards tissue engineering and regenerative medicine [1]. To this end, their mechanical properties under dry as well as wet conditions were subsequently investigated [2]. Upon wetting, these aerogels showed strong stiffening in their mechanical behavior. In this work, a micromechanically motivated model approach to describe this phenomenon is proposed. The nanofibers in the aerogel network are considered to undergo structural rearrangement upon being subjected to water. Furthermore, the collapse of the micropores (pore diameter below 5 nm) results in the formation of local hydrogel-like network phase. The constitutive model is based upon the assumption that the total network can be decomposed into a hydrogel-like network and a restructured aerogel network. The aerogel network is described based on the micromechanical model proposed by Rege *et al.* [3], while the hydrogel-like network is modeled based on the phenomenological approach of Gent [4]. This first approach towards modeling shows reliable results against the experimental stress-strain curves of alginate-starch aerogels [5].

1 Motivation

The past two decades have seen a surge in the amount of publications on biopolymer aerogels. They are highly nanoporous biomaterials that are characterized by a very low bulk density, biocompatibility, and biodegradability. Importantly, biopolymer aerogels are able to re-swell in aqueous media yielding original hydrogels. Therefore, they can be seen as a dry form of hydrogels, which retain mesoporous nature of the starting pristine hydrogels. These features have rendered biopolymer aerogels very attractive for tissue engineering applications, where mechanical performance of dry, partially and fully hydrated aerogels should be fine tuned to meet specific requirements. While mechanical behavior of dry and fully hydrated aerogels is extensively studied, only fragmental knowledge exists on mechanical performance of partially wetted biopolymer aerogel networks. This contribution intends to bridge the gap.

2 Experimental Findings

Antonyuk *et al.* [2] first tested the mechanical behavior of alginate-starch aerogels under wet conditions and reported a pronounced stiffening effect. The hydration mechanism of gelatin containing hybrid aerogels have recently been investigated by using a combination of nuclear magnetic resonance (NMR) spectroscopy and small angle neutron scattering (SANS) techniques [6]. In general, liquid state NMR spectroscopy is able to support information on the localization, chemical environment and transport of water molecules in hydrated biopolymer aerogels. The NMR relaxation times of protons in water molecules are informative on the extensions of hydration spheres. The geometry and the size of water droplets and puddles forming in the focal points of the solid backbone can be investigated by NMR cryoporometry. The self-diffusion properties of water, supplied by PGSE NMR measurements, give information on the confinement of water molecules and the permeability of the hydrated pore network. The hydration induced rearrangement of the aerogel backbone and the consequent alteration of the porous structure can be investigated by using SANS and solid state NMR spectroscopy. The compilation of the data supplied by these diverse techniques makes it possible to understand the hydration mechanism and the complicated hydration induced structural changes in biopolymer aerogels. Such experiments have recently been performed in the case of alginate-based aerogels that show the significant rearrangement of the aerogel backbone due to its hydration and the formation of extensively hydrated regions in the focal points of the solid network.

3 Modeling perspective

To theoretically describe the observed stiffening effect in biopolymer aerogels under wetting, Rege *et al.* [5] proposed a network decomposition-based model approach, where the material network was decomposed into a hydrated aerogel one and

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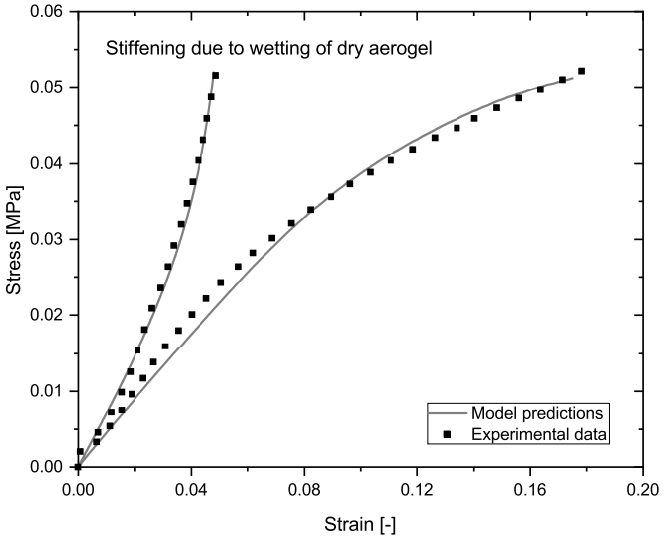

Fig. 1: Model predictions *vs*. experimental data of alginate-starch aerogels subject to wetting. The experimentally seen stiffening effect can be quantified by means of the proposed model approach. The curves are based on [5].

a hydrogel-like one. Biopolymers carry bound water which is retained after moderate drying. This makes the surfaces of biopolymers more hydrophilic. An avalanche-like adsorption at the sites where the bound water is presents is expected, since the –OH groups serve as both donors and acceptors. This results in local accumulation of the water along with hydration of the polymer backbone. It is common to model the hydration mechanism of biopolymers assuming two networks, a hydrogel-like one and a dry one, derived from the original backbone. Thus, available experimental and literature data support the idea of the formation of local hydrogel clusters within the aerogel body. This cluster formation is considered to begin at the smaller pore (micropores) sites, *i.e*. at the focal points of the aerogel network.

The restructured aerogel network was modeled based on the microcell model proposed in [3] while the hydrogel-like network was modeled by means of the Gent model [4]. The total network strain energy is then the sum of the aerogel network energy and the hydrogel-like network energy. The model predictions *vs*. the experimental data of dry and wet alginate-starch aerogels is illustrated in Figure 1. The model approach shows very good agreement with the experimental data. However, the Gent model is a phenomenological one, and for describing the local hydrogel-like cluster formation by means of a physically motivated model, further investigations into the microstructure of the network are necessary.

4 Conclusions

Recent experimental evidences support the network decomposition-based model ansatz for describing the mechanics of aerogels upon wetting. The resulting model predictions are in very good agreement with the experimental findings for the case of alginate-starch aerogels. The newly proposed approach paves the way forward towards advancing the understanding of the hydration mechanism in biopolymer aerogels.

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