Multilayered Hydrogels with Tunable Hierarchical Structures

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1. Introduction

Hydrogels are a class of tissue-mimicking, high-water-content polymeric materials, which normally produces an isotropic structure [1]. In contrast, natural structural materials such as, ligament, cartilage, bone, cornea, fish scales *etc*. are mostly composed of highly ordered microscale fibrous lamellars and therefore, exhibit excellent functionalities [1]. Until now, several advanced methods have been developed to produce highly aligned polymer orientation in hydrogels, however those methods cannot be applied to produce programmable hierarchical structures in bulk hydrogels [2].

Cellulose, a most abundant naturally occurring biopolymer on earth, has recently been used for the design of structural biomaterials in view of its multiple favorable properties, such as rigid structure, high strength, low-cost, hydrophilicity, biofunctionality, biodegradability, and non-toxicity [3]. Natural structural materials exhibit unique combinations of superior mechanical properties (strength, stiffness and toughness) because they are composed of rigid biopolymers with highly ordered hierarchical structures and robust interfacial design [4]. Inspired by the hierarchical design of natural materials, we have developed herein a bottom-up method based on a robust self-welding strategy to fabricate multilayered cellulose hydrogels with programmable polymer orientation (Fig. 1). Each layer in the multilayered hydrogels contains highly aligned polymer orientation. The welding strategy reported herein connects those layers with robust bonding through an interfacial reconfiguration process, allowing full integration without compromising the highly aligned polymer structure. This fabrication strategy allowed us to create multiple types of orientation patterns including parallel and orthogonal layer, axial and concentric rolling in the multilayered hydrogels (Fig. 1).

The multilayered hydrogels (water content: ~68 wt%) exhibit excellent mechanical properties along the polymer direction with Young's modulus of ~140 MPa, tensile strength of ~47 MPa, work of extension of`~20 MJ m^{-3}; representing strongest high-water-content (>65 wt%) hydrogel reported ever. Due to the internal ordered structure, the multilayered hydrogels exhibit strong anisotropic mechanical property, anisotropic conductivity and 3D shape changing phenomena.

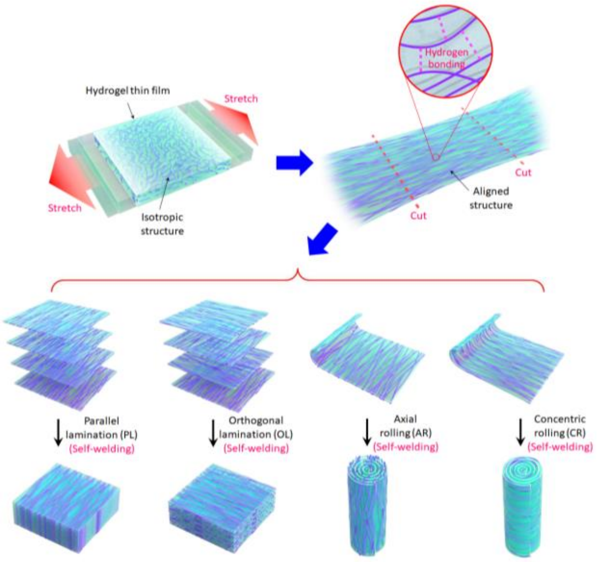

Fig.1 A novel pathway for designing multilayered hydrogels with tunable hierarchical structures using a self-welding-based interfacial reconfiguration process.

2. Fabrication and characterizations

Our method includes three fabrication steps. In the first step, low-thickness (~0.5 mm) cellulose hydrogel films were fabricated from a precursor solution of cellulose prepared by dissolving 1.5 g cellulose paper in 98.5 g *N*,*N'*-dimethylacetamide (DMAc)/lithium chloride (LiCl) [92:8] solvent.

In the second step, polymers in cellulose hydrogels were aligned *via* a prestretching method.

In the third step, Anisotropic cellulose hydrogels (thickness: ~0.25 mm) were bonded strongly using our welding method to obtain multilayered hierarchical hydrogels. Hydrogel films were equilibrated in DMAc. Each layer of the organogel was soaked in the cellulose/LiCl/DMAc solution for 30 s before they were joined together to prepare multilayered hydrogels. The 6-parallel-laminate (6PL) and 6-orthogonal-laminate (6OL) gels were prepared by stacking six layers of cellulose-soaked gels in parallel (i.e., the polymers in each layer were oriented in the same direction) and orthogonally (i.e., the polymers in adjacent layers were oriented perpendicular to each other), respectively (Fig. 1). Axially rolled (AR) and concentrically rolled (CR) hydrogels were prepared by rolling a hydrogel film along the width (the dimension in which the cylindrical axis is aligned with the polymers of the layer) and length (the dimension in which the polymers of the layer are arranged concentrically around the cylindrical axis) directions of the sample, respectively (Fig. 1). The multilayered gels were then kept in air for 1 d. All the adjacent layers connected with each other through strong H-bond formation among the reorganized cellulose networks. The solvents of the self-bound multilayered gels were then sequentially replaced with ethanol and water to obtain the final 6PL, 6OL, AR and 6OL hydrogels.

The structure of the hydrogels was characterized by polarizing optical microscopy, scanning electron microscopy, and X-ray diffraction analyses. The mechanical properties were studied in details by tensile, compression, and cyclic loading-unloading testing. The adhesive strength was determined by lap-shear test. The conductivity was determined by resistance measurements.

3. Results and discussion

Water content of all the multilayered hydrogels was ~68 wt%, which is very similar to the biological tissues such as skin, cartilage and ligament [5]. The layers in the self-welded multilayered hydrogels were bonded strongly. The adhesive strength between two cofacially jointed lamellas was determined to be 0.83 MPa using the standard lap shear test; this value is close to the cartilage-bone adhesive strength. Each layer contained highly aligned polymer orientation. The birefringence of prestretched cellulose hydrogel films is as high as it surpassed that of highly ordered native tissues, such as corneas, muscles, and tendons. Such oriented structures led to strong anisotropic mechanical properties (Fig. 2). Along the polymer direction (//) the maximum Young's modulus, tensile strength and work of extension of 6PL hydrogel were 118 MPa, 46.5 MPa and 21.1 MJ m^{-3}, respectively; the properties were higher than those in perpendicular direction by factors of ~11, ~12 and ~4, respectively. The mechanical properties of the hydrogels were highly tunable based on the polymer orientation of each type of multilayered hydrogels (Fig. 2).

Due to the highly ordered structures, the multilayered hydrogels showed anisotropic electrical conductivity. Along the polymer direction the conductivity is almost double to the corresponding value at perpendicular to the polymer direction.

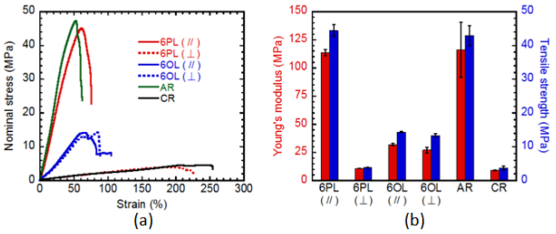

Fig. 2 (a) Tensile stress-strain curves of 6PL, 6OL, AR and CR hydrogels. (b) Comparison of Young's modulus and tensile strength of different multiayered hydrogels.

4. Conclusions

In summary, we have developed various types of multilayered cellulose hydrogels with tunable structures and mechanical properties by integrating three unique properties including, a) high mechanical properties of the constituent thin layer hydrogel, b) stress-induced highly aligned structure, and c) robust self-welding using the same material constituent. This work presents a novel pathway for designing multilayered hydrogels with tunable hierarchical structures, and the resulting hydrogels exhibit multiple functionalities including a combination of superior mechanical properties, with strong mechanical and electrical anisotropy, and orientation dependent shape changing phenomenon, which will find numerous biomedical and technological applications.

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