Morphology and formation mechanism of oriented multi-layer chitosan hydrogel

Jingyi Nie, Zhengke Wang, Qiaoling Hu

MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

Introduction

Hydrogels, in most cases, are homogeneous materials and are considered for their bulk properties. However, hierarchical soft material exhibiting organization at different scales can be a prerequisite for bio-related applications. In this work, oriented structure was constructed in multi-layered CS hydrogel without any auxiliary crosslinking agent. The formation of layers can be explained by the Liesegang ring phenomenon. The introduction of orientation endowed multi-layered hydrogel with orderliness in another direction. The present work focused on structural characteristics in 3-dimensions and the formation mechanism of orientation

Results and Discussion

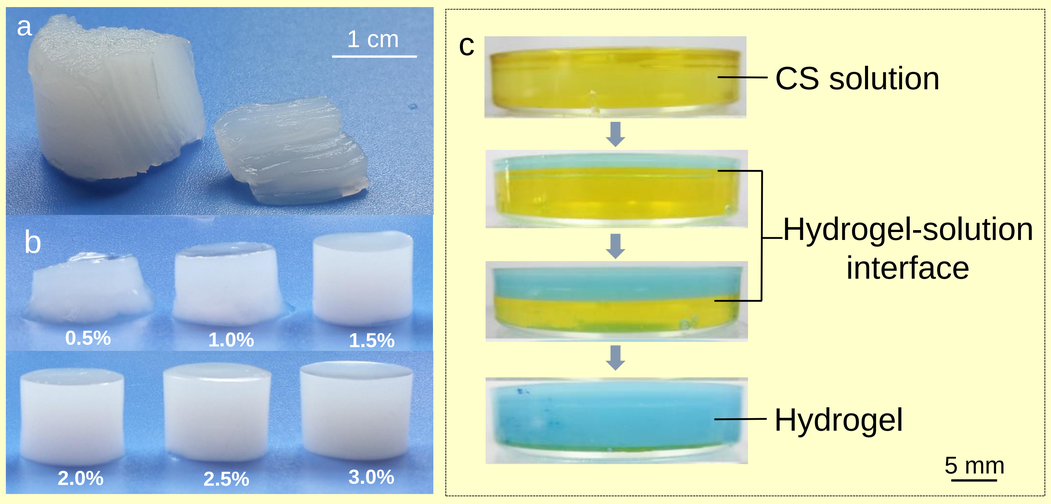


Figure 1 | Digital photographs of CS hydrogel (**a**) Orientation; (**b**) CS hydrogels with different *c*(CS);(**c**) gelation process at different reaction time. Solution and hydrogel were colored by bromothmol blue for visibility. In view of pH range, the blue part corresponded to hydrogel already formed while the yellow part corresponded to unreacted solution, and the boundary indicated the hydrogel-solution interface.

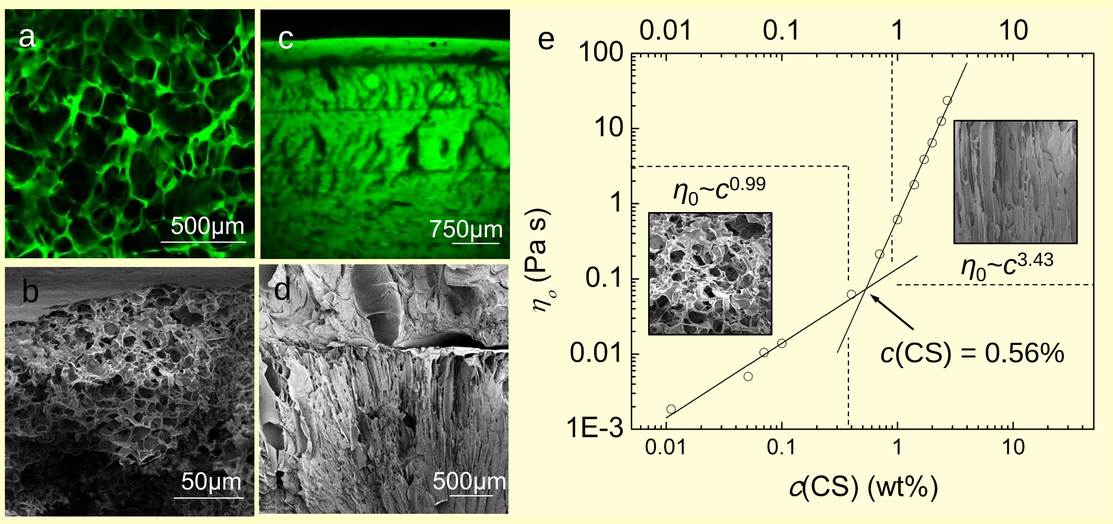


Figure 2 | Morphology of hydrogel and relationship between morphology and entanglement. (**a**) CLSM image, *c*(CS)=0.1 wt.%, cross; (**b**) SEM image, *c*(CS)=0.5 wt.%, longitudinal; (**c**) CLSM images, *c*(CS)=4.0 wt.%, longitudinal; (**d**) SEM images, *c*(CS)=3.0 wt.%, longitudinal;(**e**) Dependence of zero-shear viscosity (η_o) on *c*(CS) at 25 °C.

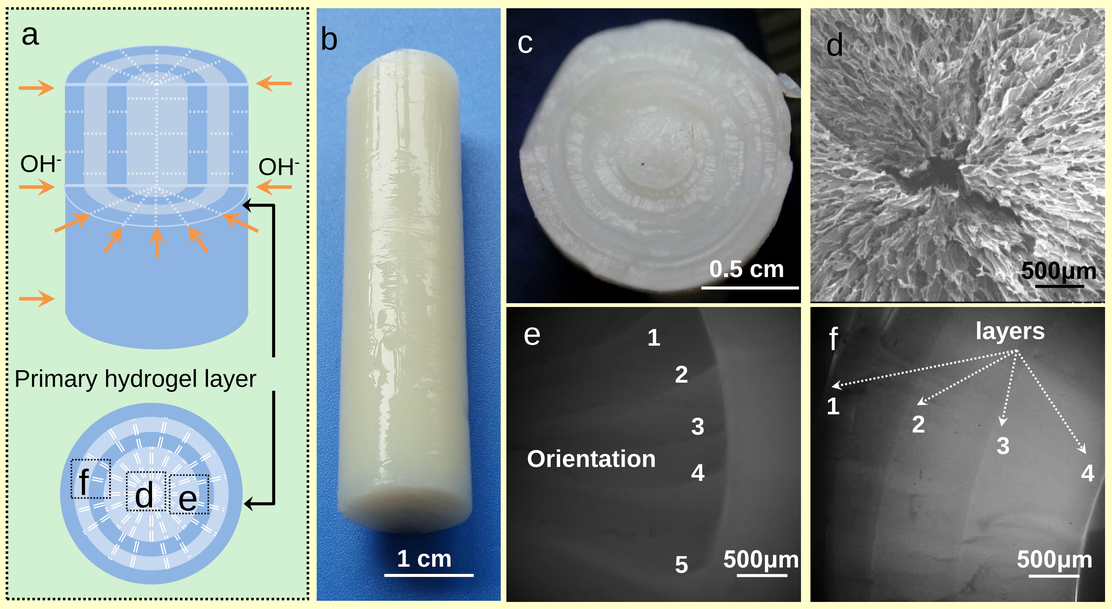
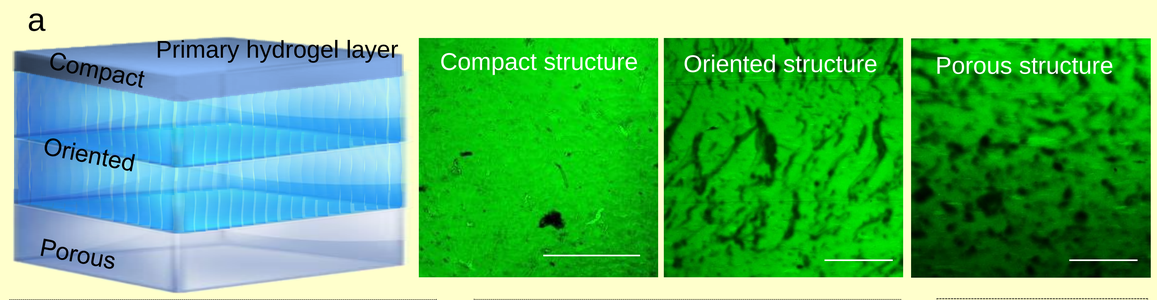


Figure 3 | Hydrogel prepared by cylindrical mold. (**a**) Schematic; (**b**)-(**c**) cylindrical hydrogel, overall view and cross section, respectively; (**d**)-(**f**) Morphology of hydrogel at different positions; positions were marked out in (**a**) with corresponding letters.



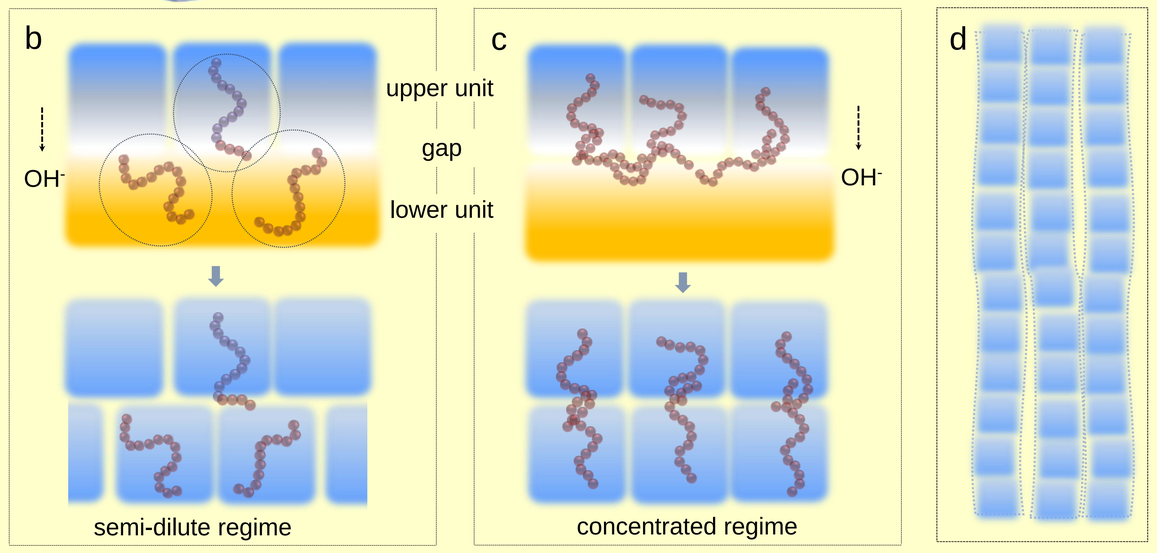


Figure 4 | Schematic model of layered-oriented CS hydrogel and illustration of formation mechanism. (**a**) Schematic model, CLSM images corresponding to compact region, oriented region and porous region, respectively, *c*(CS) >1.0 wt.%, scale bar represented 100μm. (**b**)-(**d**) Macromolecular interactions in "gel-sol consecutive reaction units" during the gelation process, (**b**) semi-dilute regime, (**c**) concentrated regime, and (**d**) formation of oriented structure by stacking of reaction units.

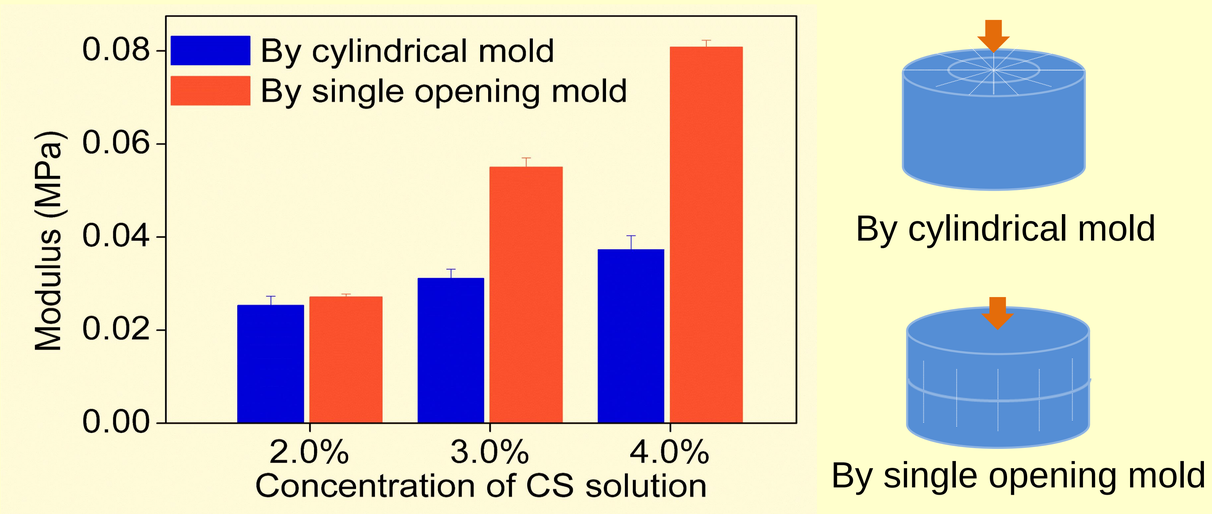


Figure 5 | Mechanical property of CS hydrogels. Modulus of hydrogel samples prepared by different molds, which possessed different directions of orientation, *c*(CS)=3.0 wt.%;

Conclusion

The gelation process of solubilized CS in acidic aqueous medium possesses a layer-wise characteristic, which contributes to unique layered-oriented structure in resulted hydrogel. Hydrogels prepared this way share structural characteristics: multi-layer structure parallel to the isopleths of *c*(OH^-), and oriented structure formed along the diffusion direction of OH^-. Sufficient entanglement of macromolecular chains and proper diffusion rate of hydroxyl ions are two vital requirements in the formation of organized structure.

Reference

- Ladet, S., David, L. & Domard, A. Multi-membrane hydrogels. *Nature* **452**, 76-U76, (2008).
- Yan, K. *et al.* Coding for hydrogel organization through signal guided self-assembly. *Soft Matter* **10**, 465, (2014).

Acknowledgement

National Natural Science Foundation of China (Nos. 21104067, 21274127 and 21374099)

Please feel free to contact me: Jingyi.nie@163.com