Cellulose nanofiber-based hydrogels with improved mechanical properties

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Hydrogels are wet and soft materials, comprising hydrophilic polymer networks, which hold large amounts of water and have similar wet properties to human tissues. One of the most important issues for synthesized hydrogels is to improve the mechanical properties. Cellulose nanofibers (CNFs) are hydrophilic natural materials, which are extremely stiff and strong and are thus widely used to reinforce hydrogels. However, problems remain. First, the stiffness of CNFs in wet conditions is lost because of disengagement of interfibrillar hydrogen bonds. Second, it is difficult to increase the CNF content owing to the high viscosity. Third, the interactions between CNFs and the polymer matrix are weak under wet conditions. Therefore, we recently tried to composite a wet CNF cake, which has a high CNF content, with polymers to fabricate composite hydrogels with improved mechanical properties.

CNF/poly(vinyl alcohol) hydrogels [1]

It will be convenient if CNFs can be combined with polymer directly to prepare hydrogels. Poly(vinyl alcohol) (PVA) is considered because PVA is a water soluble, crystallizable, biodegradable and nontoxic polymer with good mechanical properties, even in a hydrated state. In detail, a CNF suspension with a concentration of 0.1 wt% was filtrated to form a CNF cake with a solid content of around 10 wt%. Then, CNF/PVA hydrogels were prepared by immersing the CNF cake in PVA aqueous solution followed by the treatment of drying, annealing and rehydration. The resulted sample, with a water content of 66.8%, had an elastic modulus and fracture strength of 47.92 ± 0.99 MPa and 15.91 ± 0.48 MPa, which were almost comparable to skin and cartilage (Fig. 1). It was revealed that both the PVA networks and the interactions between the CNFs and PVA were maintained well in the hydrated state. This study may suggest a simple and versatile method for preparation of load-bearing hydrogels from nanocelluloses.

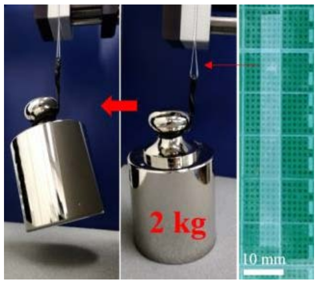

Fig. 1 CNF/PVA hydrogels. A small hydrogel sheet with width of 5 mm and thickness of 0.25 mm could hold a 2-kg weight.

Modified CNF-based hydrogels [2]

We also used the surface modified CNFs to prepare hydrogels, expecting to improve the interactions between CNFs and polymer matrix. To simplify the modification process, we used a CNF cake as a reactor, where nanochannels formed with a large aspect ratio. The flow in the nanochannels under the force of a vacuum might show a negligible back-mixing phenomenon. When the reactant was filtrated through, the water in the CNF cake was replaced by the reactant mixture gradually and the reaction occurred. After the reaction, the cake was washed by passing ethanol and water through the cake. As a result, the degree of substitution of maleic acid monoester-modified CNFs reached 0.14 at room temperature within 25 min. The crystallinity and morphology of modified CNFs were well maintained. Then, the modified CNFs were used to form composites with poly(acrylamide-co-acrylic acid) networks, which were further cross-linked by Fe^{3+}. The elastic modulus of the nanocomposite hydrogels increased considerably from 10.27 ± 0.48 MPa to 24.67 ± 0.53 MPa after slight surface modification. The additional cross-linking enhanced the friction force between nanofibers and matrix, resulting in increased modulus. Our modification method is simple but effective. It shows potential for preparing a range of CNF-based functional nanocomposite materials. The stiffened composite hydrogels also proved the importance of interfacial design for CNF-based hydrogels.

References

[1] X. Yang, K. Abe, S. K. Biswas and H. Yano, *Cellulose*, 2018, 25, 1-10.

[2] X. Yang, S. K. Biswas, H. Yano and K. Abe, *ACS Sustainable Chemistry & Engineering*, 2019, 7, 9092-9096.