# ABSTRACTS (PH D THESIS)

## Strong cellulose nanofiber composite hydrogels via interface tailoring

**(Graduate School of Agriculture,
Laboratory of Active Bio-based Materials, RISH, Kyoto University)**

**Yang Xianpeng**

Cellulose, the most abundant biomass, has been commercially available in diverse fields, while the application of cellulose in the nanoscale is not yet widely commercialized. This study is to explore the application of cellulose in the nanoscale. Hydrogels are highly hydrated polymer networks, and have great potential in many areas, such as artificial tissues and soft bioelectronics. In many cases, hydrogels require load-bearing properties, however it is still challenging to obtain simultaneously tough and strong hydrogels. Nanocelluloses possess many advantages to reinforce hydrogels, including good hydrophilicity, impressive strength and stiffness, high specific surface area, and tunable surface chemistry. However, the reinforcement is limited: (1) the concentration of nanocellulose is low; (2) the nanocellulose-matrix architecture is scarcely designed. To solve above problems, cellulose nanofibers (CNFs), mechanically disintegrated from wood powders, were used to fabricate composite hydrogels. First, it is easy to filtrate CNF suspension to form a wet cake with a high CNF concentration. The obtained CNF cake, with layered structures, is expected to be composited with polymer networks. Second, the surfaces of CNFs are covered with hemicellulose which is more reactive than cellulose. The interfacial interactions between CNFs and polymer networks may be precisely fabricated.

In Chapter 2, CNF/poly(vinyl alcohol) (PVA) hydrogels were prepared via direct blending. In brief, a wet CNF cake was immersed into PVA solution with various concentrations to absorb PVA chains, followed by drying-annealing and rehydration processes. The CNF/PVA hydrogels showed comparable elastic modulus and fracture strength to skin and cartilage. In addition, the CNF/PVA hydrogels had a high water content and showed high fracture energy.

In Chapter 3, poly(acrylamide-co-acrylic acid) networks were incorporated into CNF cakes via in situ polymerization, followed by ionic cross-linking with $Fe^{3+}$. This method also resulted in simultaneously stiff, strong and tough hydrogels. Compared with the blending method in Chapter 2, the method of in situ polymerization was applied to diverse monomers, presenting versatile features. Based on the results of Chapter 2 and Chapter 3, it was proved that a wet CNF cake was an appropriate start material for strong and tough composite hydrogels. The polymer networks should have good compatibility with CNFs and be easily cross-linked.

In Chapter 4, the surfaces of CNFs were modified to enhance the interfacial interactions between CNFs and matrix. The reaction of CNFs and maleic anhydride, using a CNF cake as a reactor, was examined. The water in the CNF cake was readily replaced by filtrating a mixture of solvent and reactant through the cake. At the same time, the reaction between the CNFs and reactant mixture occurred. This new modification method, inspired by the fluid in a plug flow reactor, was effective and convenient. Then, the polymer networks, which were the same as Chapter 3, were fabricated in the modified CNF cake. The composite hydrogels were indeed stiffened owing to the enhanced interfacial interactions, although the toughness was reduced.

In Chapter 5, a new method of grafting polymers from CNFs was developed. Various vinyl polymers, including hydrophobic and hydrophilic polymers, were grafted from CNFs via UV irradiation in the absence of an initiator. It is assumed that the primary free radicals were generated on the surfaces of CNFs (Figure 1). The hydrophilic-hydrophobic properties of CNFs were readily adjusted after polymer grafting while the crystalline structure of CNFs was retained. This green and effective method was called UV grafting.

In Chapter 6, polyacrylamide was grafted on CNFs via UV grafting to form a composite hydrogel, which resulted in toughened property in contrast to the initiator-based sample. It was confirmed that UV grafting was a powerful tool prepare CNF composites with a nanofiber/grafted matrix architecture and

excellent features. In addition, the surface chemistry of CNFs played an important role in the process of grafting.

In Chapter 7, poly(2-hydroxyethyl methacrylate) was grafted on CNF via UV grafting to form a composite hydrogel which presented strain-stiffening, strong and tough properties. The stain-stiffening behavior was ascribed to the synergistic alignment of CNFs and rearrangement of polymer networks. Double grafting was used to enhance the stain-stiffening behavior. It is believed that multiple UV grafting can result in diverse CNF/matrix architectures.

The main findings of this study are summarized as follows: (1) incorporating polymer networks into a CNF cake was an effective approach to prepare stiff, strong and tough composite hydrogels; (2) interfacial interactions between CNFs and matrix were tailored by surface modification and polymer grafting; (3) the plug flow reactor method simplified the chemical modification of CNFs; (4) UV grafting was a powerful method to graft vinyl polymers on CNFs and prepare composite hydrogel with excellent features.

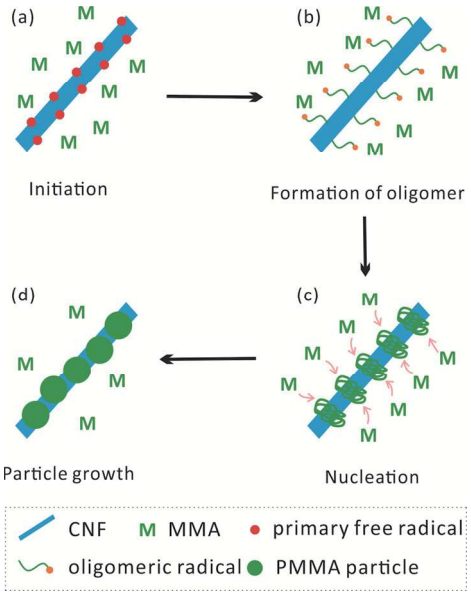


Figure 1. Possible process of UV grafting

**Acknowledgements**

I am sure I would never forget these words: do not care about what others are doing and do your own research. This is only one of innumerable golden sayings I learned from my supervisors, Prof. Yano Hiroyuki and Dr. Abe Kentaro. I really appreciate what they have done for me and what they have taught me in the past three years. I also wish to express my sincere appreciation to Prof. Wada Masahisa and Prof. Tsujii Yoshinobu, who offered valuable comments and suggestions on my thesis and researches. The Laboratory of Active Bio-based Materials (LABM) is the most ideal lab I have seen. This is an open lab where I feel very relax and can focus on research. This is a creative lab where I am inspired and excited every day. This is a future-oriented lab where I can understand the values of research. I become much more confident and I hope that I can continue the research at least the next 40 years, just like Prof. Nakatsubo Fumiaki. All the members in the lab are so friendly that I am really inspired to transfer the kindness to others. I could not finish this thesis without the understanding, support, encourage of my family. Words can't express my thanks to my mother (Yang Yuyun), father (Yang Mingde) and wife (Wu Jiaping). I also appreciate the Kato Asao International Scholarship Foundation, not only for scholarship, but access to Japanese culture.

**References**

[1] Yang, X.; Abe, K.; Biswas, S. K.; Yano, H., Extremely stiff and strong nanocomposite hydrogels with stretchable cellulose nanofiber/poly(vinyl alcohol) networks. *Cellulose* 2018, *25* (11), 6571-6580.

[2] Yang, X.; Biswas, S. K.; Yano, H.; Abe, K., Fabrication of ultrastiff and strong hydrogels by in situ polymerization in layered cellulose nanofibers. *Cellulose* 2020, *27* (2), 693-702.

[3] Yang, X.; Biswas, S. K.; Yano, H.; Abe, K., Stiffened Nanocomposite Hydrogels by Using Modified Cellulose Nanofibers via Plug Flow Reactor Method. *ACS Sustainable Chemistry & Engineering* 2019, *7* (10), 9092-9096.

[4] Yang, X.; Ku, T-H.; Biswas, S. K.; Yano, H.; Abe, K., UV grafting: surface modification of cellulose nanofibers without the use of organic solvents. *Green Chemistry* 2019, *21* (17), 4619-4624.