



Stretchable composite hydrogels incorporating modified cellulose nanofiber with dispersibility and polymerizability: Mechanical property control and nanofiber orientation



Ryosuke Kobe ^a, Shinichiro Iwamoto ^b, Takashi Endo ^b, Kouzou Yoshitani ^c,
Yoshikuni Teramoto ^{c,*}

^a Graduate School of Applied Biological Sciences, Gifu University, Gifu 501193, Japan

^b Research Institute for Sustainable Chemistry, Department of Materials and Chemistry, National Institute of Advanced Industrial Science and Technology (AIST), Higashi-Hiroshima, Hiroshima 7370046, Japan

^c Faculty of Applied Biological Sciences, Gifu University, Gifu 501193, Japan

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ABSTRACT

We fabricated composite hydrogels using surface-modified cellulose nanofiber (CNF) as a multifunctional crosslinker and *N*-isopropylacrylamide (NIPAM) as a monomer. Surface modification of CNF was performed using maleic anhydride (MA), which endowed the CNF with not only aqueous dispersibility but also vinyl polymerizability. We characterized the MA-modified CNF (MACNF) using wet chemical analysis, spectroscopy, and morphological observations. Hydrogels were prepared by *in situ* radical polymerization of mixtures of MACNF aqueous suspensions and NIPAM monomer, using a radical initiator and a catalyst under various conditions. The obtained hydrogels were transparent and highly stretchable (to more than 20 times their original length), and their mechanical properties, in particular, their tensile strength, could be controlled by exploiting the high dispersibility of the MACNF. Optical anisotropy measurements of the stretched gel specimens revealed that the MACNF fibers were highly oriented due to the large deformation, which led to an increase in the tensile strength of the specimens. A clear temperature dependence of the optical transmittance of the hydrogel samples was also observed, which originates from the coil-to-globule transition of poly(NIPAM) in aqueous media at its lower critical solution temperature.

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1. Introduction

Cellulose nanofiber (CNF) attracts considerable attention in the broad field of material science and technology [1]. One of the key approaches employed to expand CNF applications is material functionalization by incorporating CNF into a diverse range of composite materials [2–8]. Previous studies [9,10] have demonstrated highly compatible composites and interpenetrating networks (IPNs) of cellulose/synthetic polymers using suitable solvents. The IPNs were formed by a chemical blending technique involving solution coagulation and bulk polymerization [11–13].

In recent years, several significant achievements [14–18] have further progressed the IPN concept for the structural design of gel

networks; in particular, a nanocomposite (NC) gel was synthesized by Haraguchi and coworkers by *in situ* polymerization of a vinyl monomer in the presence of clays with an abundance of vinyl groups as a multifunctional polymer crosslinking agent [17,18]. In the NC gel, the inter-crosslinking molecular weight (i.e., the chain length between crosslinking points) was large, and its distribution was narrow. By extension, the flexible polymer chains between the clay sheets in the NC gels have the ability to be extensively elongated and reversed without breaking. NC-type composite materials based on nanocelluloses have also been proposed by several groups [19,20].

In our preceding study, we succeeded in fabricating rarely reported CNF-based stretchable materials (composite hydrogels) using surface-modified CNF as a multifunctional crosslinker [21]. The CNF was modified to introduce polymerizable vinyl groups onto its surface by silane coupling. We subsequently conducted *in situ* radical polymerization of mixtures of modified CNF aqueous

* Corresponding author.

E-mail address: teramoto@gifu-u.ac.jp (Y. Teramoto).

suspension and *N*-isopropylacrylamide (NIPAM) monomer using a radical initiator and a catalyst. The obtained composite hydrogels (0.005–0.1 wt% modified CNF concentration and ~90 wt% water content) could be elastically stretched to more than 700 times their original length, which was attributed to a long poly(NIPAM) (PNIPAM) chain length between crosslinking points [18]. However, it was difficult to vary the mechanical properties of the hydrogels because of the poor dispersibility of the modified CNF in water. We thus devote efforts toward accomplishing control of the mechanical properties of CNF-based composite hydrogels in the present study.

Very recently, Iwamoto and Endo reported highly dispersible 3-nm-thick lignocellulose nanofibers obtained from wood esterified with maleic anhydride (MA) [22]. The good dispersibility was attributed to the repulsion between the negative surface charges of MA moieties that were introduced by the esterification. Interestingly, because MA possesses an unsaturated C=C bond, it could potentially be incorporated into vinyl polymerization. Accordingly, we expect that MA is a very suitable reagent for introducing both dispersibility and polymerizability to CNF, which should enable the fabrication of composite hydrogels via *in situ* polymerization of monomers in the presence of a modified CNF (MACNF) crosslinker, as shown in Scheme 1.

In the present study, we investigated the possibility of improving the aqueous dispersibility of CNF by surface modification with MA, and characterized the surface modification through titration, spectroscopy, and microscopy. The polymerized hydrogel product lost fluidity and showed high transparency and stretchability. We could control the tensile mechanical properties of the hydrogels by varying the MACNF concentration of the highly dispersed MACNF in water. Birefringence measurements indicated that the MACNF component of the stretched hydrogel specimens was highly ordered. Therefore, the improvement in tensile strength was likely due to the sustainer effect of the highly aligned MACNF fibers in the extended hydrogels. A clear dependence of the optical transmittance of the hydrogels on temperature was also observed, which originates from the intrinsic coil-to-globule transition of PNIPAM in aqueous media at its lower critical solution temperature (~32 °C) [23].

2. Experimental section

2.1. Materials

CNF (BiNF-i cellulose, WMa-10002) was obtained as a 2 wt% water dispersion from Sugino Machine, Ltd., and its features according to the manufacturer were as follows: average fiber diameter, 20–50 nm; degree of polymerization (DP) of cellulose, 650; viscosity, 3000 mPa s (25 °C). *N,N*-Dimethylacetamide (DMAc) and NIPAM were purchased from Wako Pure Chemical Industries, Ltd. DMAc was dried with potassium hydroxide pellets before use. NIPAM was recrystallized from *n*-hexane twice and then dried under vacuum at 30 °C for 1 h. Other reagents were obtained from Wako Pure Chemical Industries, Ltd., and used without further

purification.

2.2. Surface modification of CNF

As-provided 2 wt% CNF aqueous suspension (120 g) was continuously solvent-exchanged using acetone and DMAc at room temperature. Reaction of the obtained suspension in DMAc (2.4 g CNF in 200 mL) and maleic anhydride (MA, 100 g) was conducted in a four-necked flask equipped with a mechanical stirrer at 120 °C in an oil bath under a nitrogen flow (200 mL/min) for 3 h. The resulting dispersion of the reaction product (MACNF) was subjected to successive solvent exchange with acetone and deionized water to remove DMAc solvent and unreacted reagent from the system. The obtained aqueous dispersion was neutralized with 1 M NaOH aqueous solution. The neutralized dispersion was further purified by dialysis in deionized water for 1 week at room temperature. The dispersion was then passed through a high-pressure homogenizer (Masscomizer X, Masko Sangyo Co., Ltd.) three times at 200 MPa. The MACNF aqueous dispersion was dialyzed in 7 wt% PEG aqueous solution for three days to obtain a concentrated MACNF/water dispersion. MACNF aqueous dispersions of various concentrations for use in hydrogel synthesis were prepared by re-dispersing the concentrated dispersion in deionized water using a physical homogenizer (Phycotron NS-20G/20P, Microtec Co., Ltd.) and an ultrasonic homogenizer (US-150E, Nissei Co.).

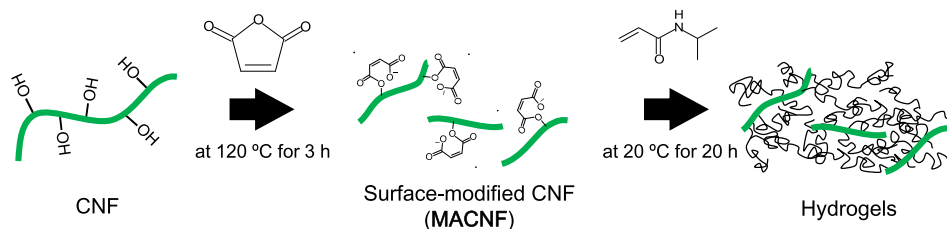
2.3. Synthesis of hydrogels

We first prepared transparent dispersion mixtures composed of monomer (NIPAM, 3 g), crosslinker in diluent (MACNF aqueous dispersion, 26 g, various concentrations), initiator (0.03 g of potassium peroxodisulfate in 1.5 mL deionized water), and catalyst (*N,N,N',N'*-tetramethylethylenediamine, 24 μL) in a glass tube. The water content was ~90 wt% in the polymerization system. The system were stirred in an ice bath and polymerization was then performed in an ethanol bath at 20 °C for 20 h. For mechanical testing, the mixture before polymerization was transferred into a polyethylene tube (5 mm diameter) to prepare cylindrical hydrogel specimens. Throughout all of the preparation procedures, oxygen was excluded from the system by degassing, substituting with nitrogen gas, and sealing.

2.4. Characterization of surface-modified CNF

Fourier-transform infrared (FTIR) spectroscopy was performed on freeze-dried samples at the Division of Instrumental Analysis, Life Science Research Center, Gifu University. Spectra were recorded using a PerkinElmer Spectrum 100 FTIR apparatus over the wavenumber range 400–4000 cm⁻¹ at a resolution of 4 cm⁻¹ via the accumulation of 32 scans. A standard KBr-pellet method was used for all measurements and samples.

Solid-state NMR experiments were performed on freeze-dried samples of CNF and MACNF at 20 °C using a Varian FT-NMR



Scheme 1. Surface modification of CNF with MA and the following hydrogel formation via *in situ* polymerization of NIPAM.

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