



# Superporous thermo-responsive hydrogels by combination of cellulose fibers and aligned micropores



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## ABSTRACT

In the area of artificial hydrogels, simultaneous engineering of the volume transition characteristics and mechanical properties of stimuli-responsive hydrogels is an important subject. By unrestricted architecting of hierarchical structures, natural hydrogels are able to provide a wide range of swelling and mechanical properties, beyond the limits of artificial hydrogels. Herein, a combination of nanostructures and microstructures was developed to construct superporous hydrogels. Fibers of microfibrillated cellulose (MFC), an eco-friendly reinforcing material, were used as nanostructures, aligned micropores were used as microstructures, and *in situ* photopolymerization was used to immobilize the two structures together within the gel networks of poly(N-isopropyl acrylamide) (PNIPAm). The introduction of MFC distinctly enhanced volume transition, mainly by decreasing the swelling ratios above the transition. The introduction of directional micropores increased the swelling ratio below the transition and decreased the swelling ratio above the transition, thereby also enhancing the volume transition. Additionally, the formation of aligned micropores achieved fast water infiltration, which is beneficial for superabsorbent applications. The introduction of aligned micropores reduced the elastic modulus, but this could partially be compensated for by reinforcement with MFC. This combination of crystalline nanofibers and aligned micropores has great potential for the development of stimuli-responsive superporous hydrogels outperforming current artificial hydrogels.

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## 1. Introduction

Hydrogels are typically three-dimensional networks of hydrophilic molecular chains; they exhibit unique viscoelastic behaviors that can be stimuli-responsive. The most widely studied temperature-responsive hydrogel is poly(N-isopropylacrylamide) (PNIPAm), which has a lower critical solution temperature (LCST) of ca. 32 °C (Hou et al., 2008; Li, Guo, Chang, & Yang, 2012). Below the LCST, it is hydrophilic; above the LCST, its chain conformation changes to become hydrophobic. This transition causes water to be expelled, leading to a dramatic reduction in volume (JagadeeshBabu, Suresh Kumar, & Maheswari, 2011), a behavior that has been explained by hydrophobic interaction and the temperature dependence of the interaction parameter (Cho, Lee, & Cho, 2003). Because of their interesting physicochemical properties, synthetic hydrogels have many applications in various fields such as superabsorbent materials, pharmaceuticals, food chemistry, medicine, agriculture, and biotechnology (Bajpai, Shukla, Bhanu, & Kankane, 2008).

For many applications, to be useful, materials must combine high swelling (*i.e.*, high volume change) with good mechanical properties. Many natural hydrogels exemplify this combination, such as actin, which forms filament structures rather than a simple random network (Breedveld, Nowak, Sato, Deming, & Pine, 2004). In many cases, artificial hydrogels have failed to surpass the performance of natural hydrogels, because the properties of both types are largely confined by what the rubber elasticity theory predicts; that is to say, a large swelling ratio is generally accompanied by poor mechanical properties (Bhattacharyya, Guillot, Dabboue, Tranchant, & Salvetat, 2008; Zhou & Wu, 2011). To overcome this limitation, hydrogels have been engineered by architecting unique molecular chain structures, nanostructures, or microstructures. Several studies have been reported to improve the modulus and strength of hydrogels by incorporating organic or inorganic fillers such as carbon nanotubes and sodium montmorillonite layered silicates (Bhattacharyya et al., 2008; Xia, Yih, D'Souza, & Hu, 2003; Yildirim, Yin, Nair, & Sun, 2008; Zhou & Wu, 2011). Composite hydrogels have showed enhanced elastic modulus, but without notable improvement in swelling ratio (Wang et al., 2012; Xia et al., 2003).

Crystalline cellulose, an abundantly available natural polysaccharide, is a renewable material suitable for the reinforcement of composites. Pure celluloses cannot be isolated easily from plants,

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due to strong interactions with a number of associated macromolecules such as lignin, hemicellulose, and tannin (Chen et al., 2011). However, pure crystalline celluloses can be purified from bacteria, algae, and tunicates; the celluloses initially contain both highly ordered (crystalline) and less ordered (amorphous) phases (Chen et al., 2011; Martínez-Sanz, Lopez-Rubio, & Lagaron, 2011; Tischer, Sierakowski, & Tischer, 2010). Sulfuric acid hydrolysis is one of the routes to remove the disordered phases and obtain highly crystalline celluloses (Correa, Teixeira, Pessan, & Mattoso, 2010; Tischer et al., 2010). Purified microfibrillated celluloses (MFCs) 5–20 nm in diameter have been widely investigated for use as dry composites, but seldom for reinforcing hydrogels because effective load transfer is unlikely from the matrix to the MFCs. Instead, interpenetrating networks or double networks have been developed intensively (Gong, Katsuyama, Kurokawa, & Osada, 2003). However, because decreased volume transition could ensure effective load transfer, simple embedding MFC with poor load transfer could be beneficial for enhanced volume transition. Furthermore, a combination of two different structures at different scales, which mimics the hierarchical structures of natural hydrogels (Lazarides, 1976), could offer a novel strategy to engineer the properties of hydrogels outside what conventional hydrogels can offer.

Herein, MFC was used as a nanostructure for reinforcement, offering plenty of hydrogen bonding sites for 'flexible' load transfer, and well-aligned cylindrical micropores were used as microstructures to tailor swelling properties. The hypothesis was investigated that a hierarchical combination of MFC and cylindrical micropores can widen the property windows of artificial hydrogels. Cylindrical micropores were introduced and aligned by directional melt crystallization (freezing) of water along a temperature gradient. The frozen water acted as a porogen; that is, it produced porous structures. The unidirectional freezing method has been exploited for preparing various aligned porous materials, including organic, inorganic, and composite materials for bioengineering, drug delivery, catalyst supports, and separation (Nishihara et al., 2006). Recently, a combined method of directional freezing and UV-induced polymerization in a frozen state successfully fabricated anisotropic microstructures (Barrow & Zhang, 2013; Chen, Zhu, Qi, He, & Wang, 2012), which seems to be a proper method to immobilize MFC in a hydrogel matrix while simultaneously forming aligned micropores.

## 2. Experimental

### 2.1. Materials

N-isopropyl acrylamide (NIPAm) from Sigma–Aldrich (St. Louis, MO, USA) was purified by dissolution and recrystallization in n-hexane (Convertine et al., 2006). Methylenebisacrylamide (MBA) and concentrated sulfuric acid ( $H_2SO_4$ ) were used as received from Sigma–Aldrich. Irgacure 2959 (initiator) was purchased from Tokyo Chemical Industry (Tokyo, Japan). Distilled water, ethanol, and n-hexane were purchased from Duksan Chemicals (Ansan, South Korea). Kombucha was purchased from a local manufacturer (Kombucha Co., ShiHung, KyungKi, Korea); tea bags (Lipton) and food-grade sugar were purchased from a local market.

### 2.2. Preparation of MFC

A cellulose-producing bacterium was first isolated from commercially available kombucha tea, and a culture medium was prepared by adding a tea bag and 3 g of sugar to 100 mL of warm distilled water. Kombucha precursor of 1 mL was then inoculated

into the culture medium in a 1000 mL beaker and incubated at 25 °C without agitation.

A 500 g wet mat of bacterial cellulose was cut into small pieces and washed thoroughly with water to remove the odors and color of the growth medium. The mat pieces were heated at 100 °C for 3 × 25 min in 500 mL of 10% (w/v) NaOH, and then finally washed in distilled water at RT until neutral pH was reached. The pieces were then compressed into thin sheets, squeezing out as much water as possible, and the pieces were hydrolyzed for 3 days at 30 °C using 500 mL of 50% (v/v)  $H_2SO_4$ . The hydrolysis reaction was quenched by adding 500 mL of distilled water. The dispersion was isothermally centrifuged (Mega 17R+, Hanil Centrifuge, Inchon, Korea) at 15 °C and 12,000 rpm for 25 min, followed by washing with distilled water and a second centrifugation using the same conditions. The cellulose was thereby collected at the bottom of the centrifuge tube; the acidic supernatant was discarded. To remove the excess of sulfuric acid, the cellulose residue was dialyzed in distilled water until neutral pH was reached. The water was discarded, 500 mL of acetone was added, and the tube was centrifuged using the same conditions described above. MFC was obtained as a white powder by drying in a hood overnight.

### 2.3. Preparation of PNIPAm and PNIPAm/MFC composite hydrogels

To prepare PNIPAm hydrogels (designated as P), NIPAm monomer (4.42 mmol), MBA crosslinker (0.032 mmol), and initiator (0.045 mmol) were dissolved in 3.5 mL of distilled water and stirred under nitrogen atmosphere for 15 min (Singh, Kuckling, Choudhary, Adler, & Koul, 2006). An appropriate amount of monomer solution (0.9 mL) was transferred into a silicone/glass mold (5 mm thick). The mold was kept in a UV chamber (27 cm × 37 cm, 365 nm) at 5 °C. After 1 h of UV illumination, the hydrogels were soaked in 1 L of distilled water for 3 days, with daily exchange of fresh water to remove unreacted impurities.

To prepare MFC/PNIPAm hydrogels (PM), a 5 wt% MFC aq. dispersion was first prepared with magnetic stirring overnight. After ultrasonication for 5 min, appropriate amounts of monomer, crosslinker, and initiator were added for the same hydrogel composition, and the same crosslinking step described above was applied. For the preparation of PNIPAm or composite hydrogels having directional micropores (PD or PMD), the solution-filled mold was directionally frozen on top of a liquid nitrogen reservoir for 10 min and then the crosslinking step described above was applied (Fig. 2). Details on the directional freezing methods are available elsewhere (Lee & Lee, 2013).

### 2.4. Characterization

The temperature dependence of the equilibrium swelling ratio (SR) was studied gravimetrically over the 20–50 °C range with 3 °C increments. The hydrogel samples were immersed in distilled water for 4 hr at each temperature. Each sample was blotted with moistened filter paper to remove excess water and then weighed ( $W_s$ ). Five samples of each hydrogel were prepared, and the standard deviation over the 5 corresponding weight measurements was calculated. The dry weights of samples ( $W_d$ ) were obtained after freeze-drying (EYELA FDU 2200, Tokyo, Japan) followed by vacuum drying at 50 °C for 24 h. SR was defined using the following equation:  $SR (\%) = (W_s - W_d) / W_d \times 100$ .

The CP/MAS  $^{13}C$  NMR spectra of MFC fibers were collected with a VNMRS 400 spectrometer (Varian, Palo Alto, CA, USA) operating at a frequency of 400 MHz. UV–vis absorption spectra were obtained using a spectrophotometer (JASCO V-670 spectrophotometer, Japan), using samples of 1.8 mm thickness and using distilled water as a reference. To retain sample morphology

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