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Effect of surface charge content in the TEMPO-oxidized cellulose nanofibers on morphologies and properties of poly(*N*-isopropylacrylamide)-based composite hydrogels

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ABSTRACT

Owing to the higher aspect ratio and presence of negatively-charged carboxylate groups that would favorably interact with hydrophilic amide groups in poly(*N*-isopropylacrylamide) (PNIPAM) molecules, TEMPO-oxidized cellulose nanofibers (TO-CNF) is a kind of promising candidates to improve both swelling and mechanical properties of PNIPAM hydrogels. In this work, a series of TO-CNFs were isolated from inexpensive and abundant bamboo pulp to clarify effects of carboxylate contents (0.5–1.8 mmol/g) on the surfaces of TO-CNF on microstructure as well as compression and swelling properties of PNIPAM/TO-CNF composite hydrogels. An increase in the carboxylate content on the surfaces of TO-CNFs resulted in a higher degree of nanofibrillation. With increasing carboxylate content in the added TO-CNFs, the pore size of the composite hydrogels progressively became larger. It was found that the lower critical solution temperature (LCST) of PNIPAM hydrogels was independent of presence of TO-CNF and its carboxylate contents, while the equilibrium swelling ratio of PNIPAM/TO-CNF composite hydrogels below LCST were largely influenced by carboxylate contents of added TO-CNFs. The incorporation of rigid TO-CNF markedly strengthened the three-dimensional network structure of PNIPAM hydrogels, and compressive properties of the composite hydrogels were found to continuously increase with the carboxylate content in the TO-CNF. When carboxylate content of TO-CNF was 1.8 mmol/g, both compressive strength and modulus of the composite hydrogel reached 79.60 kPa and 0.97 MPa, respectively, which were 300% and 900% higher than those of pure PNIPAM one. Thus, TO-CNF appeared to be a "green" nanofiller that can simultaneously improve swelling and mechanical properties of PNIPAM hydrogels.

1. Introduction

Smart hydrogels refer to the ones which have one or more properties that can be in response to the change caused by the external stimuli, such as temperature, pH, electric field, magnetic force, etc. (Qiu and Park, 2001). Among them, poly (*N*-isopropylacrylamide) (PNIPAM) is a typical temperature-responsive one. PNIPAM hydrogels exhibit a volume phase transition around its lower critical solution temperature (LCST) of about 32 °C in an aqueous media due to the hydration/dehydration balance dominated by hydrogen-bonding interaction of hydrophilic amide groups and hydrophobic association of isopropyl groups in the PNIPAM molecules (Scarpa et al., 1967). Once the LCST is exceeded, the degree of hydration will obviously change and PNIPAM hydrogels exhibit the temperature-responsive behaviors. In addition, the response rate depends not only on their chemical structure (Varvarenko et al., 2010), but also on the formation of "skin" on the surface (Haraguchi et al., 2002) and interior micro-structure such as pore size (Spagnol et al., 2012b,c; Wei et al., 2016) and pore shape (Halake and Lee, 2014). Therefore, such a unique temperature-responsive feature of PNIPAM hydrogels makes them a very attractive candidate for a variety of applications, such as drug delivery systems (Lu et al., 2013), contact lenses (Yesilirmak and Altınors, 2013), biosensors (Yan et al., 2013), etc. However, PNIPAM hydrogels suffer from drawbacks of poor mechanical properties (e.g. elasticity) and

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slow temperature response, which largely limits its broad applications (Haraguchi, 2007; Huang et al., 2011; Miyazaki et al., 2007; Zhou and Wu, 2011). To overcome the limitations, PNIPAM hydrogels have been engineered by architecting unique molecular chain structures (Gökçeören et al., 2014; Glassman and Olsen, 2013; Haraguchi et al., 2015; Muniz and Geuskens, 2001), incorporating nanoparticles (Haraguchi et al., 2016; Ma et al., 2013; Rodrigues et al., 2014), or manipulating microstructures in the literature (Fei et al., 2012; Halake and Lee, 2014; Xu et al., 2007).

Recently, several studies have demonstrated that the incorporation of nanocellulose, a family of non-toxic and biodegradable nanofillers derived from renewable cellulose, can significantly improve swelling and mechanical properties of polymer hydrogels. Muniz et al. modified poly (acrylamide-*co*-acrylate) (Spagnol et al., 2012a) and starch-*g*-poly (sodium acrylate) (Spagnol et al., 2012c) superabsorbent hydrogels with cellulose nanowhiskers (CNWs). It was found that the addition of CNWs not only accelerated swelling equilibrium of these hydrogels, but also improved their swelling capacity. Hebeish et al. observed that the incorporation of rod-shape CNWs into PNIPAM hydrogels caused a remarkable increase in the equilibrium swelling ratio (Hebeish et al., 2014). In another study by Cha and co-workers, the addition of carboxylated CNWs increased both equilibrium swelling ratio and stiffness of PNIPAM hydrogels with pH- and temperature- sensitivities (Cha et al., 2012). By introducing microfibrillated cellulose (MFC) and micropores by directional freezing into PNIPAM hydrogels, Halake et al. developed superporous thermo-responsive hydrogels with semi-interpenetrating polymer network (semi-IPN) structure (Halake and Lee, 2014). The results revealed that the elastic modulus was improved with MFC loading and the equilibrium-swelling ratio increased with the directional micropores formed in the hydrogel. But the presence of MFC inside the hydrogel caused the equilibrium swelling ratio to drop and the formation of the directional micropores reduced the strength of the hydrogel.

In addition to CNW, cellulose nanofibibers (CNF) represents another class of promising nanocellulose materials. Unlike rod-shape and rigid CNW isolated via acid hydrolysis, CNF is usually prepared by mechanically disintegrating cellulose fiber suspensions. The latter is characterized of flexible entangled network consisting of many high-aspect-ratio and randomly distributed sub-micron nanofibers. These nanofibers consist of both individual and aggregated microfibrils made of alternating crystalline and amorphous cellulose domains, which is different from highly crystalline CNW (Dufresne, 2013). And it has been reported that CNF exhibited superior reinforcing effects on some polymeric matrices than CNW due to higher aspect ratio and entanglement between nanofibrils of the former (Siqueira et al., 2008; Xu et al., 2013). Likewise, CNF would also be another promising candidate to significantly enhance mechanical properties of PNIPAM hydrogel (Ansari et al., 2015; Kurihara and Isogai, 2015; Lu et al., 2015).

However, the sole mechanical disintegration of cellulose fibers normally suffers from intensive energy consumption for fiber nanofibrillation. Moreover, the nanofibers tend to aggregate due to strong hydrogen-bonding attraction between them. Therefore, different strategies such as chemical, enzyme and refining pretreatments, have been proposed to facilitate this process with reduced energy input. Among various pretreatments, the selective introduction of anionic carboxylate groups at the C6 primary hydroxyls of glucose unit on the cellulose microfibril surfaces through 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-mediated oxidation, turned out to be one of the most efficient and mild ones. Compared to the traditional methods (e.g. acid treatments), the recently developed method of TEMPO-mediated pre-oxidation in combination with mechanical disintegration, turned out to be one of the most mild and efficient routes to prepare CNW or CNF. The latter can overcome the disadvantages of the acid-hydrolysis method, such as relatively low yield, less higher aspect ratio, and demanding reaction conditions. Supposing that TEMPO-oxidized cellulose nanofibers (TO-CNF) was *in-situ* incorporated during the polymerization of *N*-isopropylacrylamide (NIPAM), the carboxylate groups of TO-CNF would favorably interact with hydrophilic amide groups on PNIPAM molecule chains, thereby altering swelling behavior and the mechanical properties of PNIPAM hydrogel. To the best of our knowledge, no attempts have yet been made to understand effects of carboxylate content in the surface of TO-CNF on mechanical and swelling properties of PNIPAM hydrogel. This knowledge will be crucial from the consideration of tailoring physical properties of PNIPAM hydrogel for targeted applications.

In this study, inexpensive and abundant bamboo pulp was used as a native cellulose source to disintegrate into TO-CNF with carboxylate contents varying from 0.5 to 1.8 mmol/g through a combination of TEMPO-oxidation pre-treatment and high-pressure homogenization. And the zeta potentials, light transmittance as well as morphologies of as-obtained TO-CNF suspensions were investigated, respectively. The TO-CNFs were then *in-situ* incorporated into the PNIPAM matrix during the solution polymerization and a series of PNIPAM/TO-CNF composite hydrogels was thus obtained. And the main aim of this work is to investigate effects of surface carboxylate contents in the added TO-CNFs on morphologies, compressive properties, and temperature-responsive behaviors of the PNIPAM/TO-CNF composite hydrogels.

2. Materials and methods

2.1. Materials

Bleached bamboo pulp was supplied by Sichuan Yongfeng Paper Co., Ltd (China). *N*-isopropylacrylamide (NIPAM) was obtained from TCI Development Co., Ltd. Sodium hydroxide (NaOH), 2,2,6,6-Tetramethylpiperidiniyl-1-oxyl (TEMPO), sodium bromide (NaBr), sodium hypochlorite with available chlorine of 10% (NaClO), potassium persulfate ($K_2S_2O_8$), *N,N,N′*,N′-tetramethylethylenediamine (TMEDA), *N,N′*-methylenebisacrylamide (MBA) were of chemical grade and purchased from Aldrich Chemical Co., Ltd. All other chemicals were used without further purification.

2.2. Preparation of TO-CNF

TO-CNF was isolated from bamboo pulp according to the previously reported method (Saito et al., 2006). Briefly, the dried pulp was dispersed in water using mechanical stirrer until a solid content of 2.0 wt% was achieved. Then, the desired amounts of TEMPO and NaBr (0.1 and 1.0 mmol per gram of cellulose, respectively) were dissolved into the slurry. And the oxidation was immediately initiated by adding NaClO solution. During the reaction, the pH value was maintained at 10 using 0.1 M NaOH solution. When pH value remained unchanged, the pulp fibers were filtered and then repeatedly washed with deionized water until the filtrate became neutral. Then TEMPO-oxidized fiber suspensions were subject to mechanical disintegration by successively passing through a high-pressure homogenizer (AH-BASIC, ATS Engineering Inc., Canada) for three cycles at a pressure of 1000 bar. By changing NaClO contents, three TO-CNF suspensions with varying carboxylate contents (i.e. 0.5, 1.0, and 1.8 mmol/g) were obtained. For convenience, the aqueous TO-CNF dispersions were denoted as TO-CNFx, where x represents carboxylate content in the TO-CNF.

2.3. Synthesis of hydrogels

The hydrogels with or without TO-CNFs were prepared via *in-situ* polymerization method (Cha et al., 2012; Wei et al., 2016). Typically, certain amounts of NIPAM monomer, the cross-linker