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High-water-content mouldable polyvinyl alcohol-borax hydrogels reinforced by well-dispersed cellulose nanoparticles: Dynamic rheological properties and hydrogel formation mechanism

Jingquan Han[a,b], Tingzhou Lei[c], Qinglin Wu[b,*]

[a] College of Material Science and Engineering, Nanjing Forestry University, Nanjing 210037, China
[b] School of Renewable Natural Resources, Louisiana State University AgCenter, Baton Rouge, LA 70803, United States
[c] Henan Key Laboratory of Biomass Energy, 29 Huayuan Road, Zhengzhou 45008, China

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ABSTRACT

Cellulose nanoparticle (CNP) reinforced polyvinyl alcohol-borax (PB) hydrogels were produced via a facile approach in an aqueous system. The effects of particle size, aspect ratio, crystal structure, and surface charge of CNPs on the rheological properties of the composite hydrogels were investigated. The rheological measurements confirmed the incorporation of well-dispersed CNPs to PB system significantly enhanced the viscoelasticity and stiffness of hydrogels. The obtained free-standing, high elasticity and mouldable hydrogels exhibited self-recovery under continuous step strain and thermo-reversibility under temperature sweep. With the addition of cellulose I nanofibers, a 19-fold increase in the high-frequency plateau of storage modulus was obtained compared with that of the pure PB. CNPs acted as multifunctional crosslinking agents and nanofillers to physically and chemically bridge the 3D network hydrogel. The plausible mechanism for the multi-complexation between CNPs, polyvinyl alcohol and borax was proposed to understand the relationship between the 3D network and hydrogel properties.

1. Introduction

Hydrogels are soft, viscoelastic and cross-linked (physically and/or chemically) three-dimensional networks of hydrophilic polymer that can hold large amounts of water and/or biological solution, while maintaining their structural integrity during deformation (Yang et al., 2012; Yang, Liu, Chen, Yu, & Zhu, 2008). Due to their excellent hydrophilicity, permeability, ability to mimic human tissues, hydrogels are particularly attractive in biological, pharmaceutical, and daily-care applications, such as real-time immunoassay, contact lenses, vehicles for drug delivery, cell encapsulation, implantable artificial muscles and organs, and biosensors (Sun et al., 2012; Yang, Han, Duan, Xu, & Sun, 2013). The growing environmental awareness recently has triggered interests in more environmentally friendly and biodegradable hydrogels (Zhang et al., 2011). Due to the hydroxyl groups of each repeating molecular unit, hydrophilic polyvinyl alcohol (PVA) can form chemically and/or physically crosslinked hydrogels. Most PVA hydrogels are biodegradable, highly crystalline, non-toxic, inexpensive, biocompatible, and non-carcinogenic (Asher, Kimble, & Walker, 2008; Kobayashi, Chang, & Oka, 2005; Peresin, Habibi, Vesterinen, et al., 2010). For example, a type of PVA-based hydrogel known as Salubria TM (Salumedic, Atlanta, GA) is marketed in Canada and Europe for articular cartilage replacement (Slaughter, Khurshid, Fisher, Khademhosseini, & Peppas, 2009). However, there are many applications requiring stronger hydrogels (e.g., electrochemical devices and medical implants). To enhance the mechanical strength and toughness of hydrogels, composite hydrogels have been synthesized by incorporating nanoparticles, including carbon nanotubes, metallic particles, and clay (Shin, Spinks, Shin, Kim, & Kim, 2009). These reinforcing nanofillers generally act as decelerators of propagating cracks and contribute to delaying the collapse of the composite hydrogels (Shin et al., 2009). Inspired by the recent environmental concerns, eco-friendly composite hydrogels based on renewable natural resources (e.g., cellulose, most abundant renewable natural biopolymer in nature) have assumed great significance for reinforcing various polymers. Because of the hydrophilic nature of PVA, dispersion of hydrophilic CNPs into the matrix can be readily achieved by blending an aqueous CNP dispersion with an aqueous PVA solution (Paralikara, Simonsen, & Lombardi, 2008). More importantly, cellulose exhibits a low immune response and cannot be degraded and digested in the body due to the fact that human and animal cells do not synthesize the enzymes capable of degrading cellulose (cellulases), thus cellulose reinforced hydrogels are particularly suitable for certain biomedical fields.

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* Corresponding author. Tel.: +1 225 578 8369; fax: +1 225 578 4251.
E-mail address: qwu@agcenter.lsu.edu (Q. Wu).

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In our previous study (Han, Lei, & Wu, 2013), we successfully synthesized PVA-borax hydrogels that were reinforced by well-dispersed cellulose nanoparticles (CNPs). The obtained tough, high-water-capacity (~96%), low-density (~1.1 g/cm^3), translucent hydrogels exhibited birefringence behavior and a higher transparency than the cyclic freeze–thaw prepared opaque hydrogels. Highly crystalline CNPs acted as a multifunctional crosslinking agent to physically and chemically bridge the 3D network hydrogels. By respectively incorporating three types of well-dispersed CNPs to the PVA-borax aqueous system, the mechanical strength, energy absorption and stiffness of the composite hydrogels were significantly enhanced.

Application of the hydrogels in many fields requires a fundamental understanding of their viscoelastic properties. Among those techniques that have been used to investigate the gelation kinetics of PB aqueous system, dynamic rheological techniques have attracted strong interest as a powerful and effective approach to study the supramolecular structure of hydrogels since in situ experiments are relatively facile to perform during the gelation process (Shi et al., 2012). The network structure and the cross-linking density are key factors derived from the rheological characteristics of the hydrogels (Kjøniksen & Nyström, 1996). The linear viscoelastic behavior in dynamic experiments of miscible gelling polymer systems can continuously monitor the development of cross-links (chemical and/or physical) and supramolecular complexes in hydrogel without disrupting gel structure, and they can further reflect the miscibility of polymer blends, supramolecular structure and cross-linking density of hydrogels in stages. As a result, effort has been devoted to the rheology study of PVA-borate complex aqueous systems over the past several decades (Angelova et al., 2011; Carretti et al., 2009). The effects of polymer concentration, molecular weight and temperature on the dynamic viscoelasticity of PVA in aqueous borax solutions were discussed (Koike, Nemoto, Inoue, & Osaki, 1995). The thermo-dynamic, structural, and dynamic features of cross-linked PVA hydrogels and the corresponding semidilute polymer solutions were also reported (Kjøniksen & Nyström, 1996). The crosslinking mechanism of borate ion with PVA chains was known to be a “di-diol” complexation, which was formed between one borate ion and two diol units. PB aqueous system rheologically behaved like elastic solids at high frequencies and like viscous liquids at low frequencies. The short relaxation time and small amount of energy required to break and reform the cross-links accounted for the “slime” consistency of these materials (Angelova et al., 2011). Above-mentioned studies indicate that dynamic rheology techniques can distinguish appropriate gelation conditions for the fabrication of PB hydrogels with desired properties. Regarding the industrial potential in the processing of related materials, the knowledge of the dynamic rheological behavior of PB-based system is very useful in equipment selection and quality control (Gouvea et al., 2009).

However, to the best of our knowledge, we are unaware of any reports on the gelation mechanism and rheological viscoelasticity of PVA-borax-CNP complexes in an aqueous system. For instance, the effects of different CNPs on the rheological features of PB aqueous systems have not been addressed. It is possible that the physically and chemically crosslinked hydrogels can exhibit some unique viscoelastic properties. The objectives of this study were to characterize the dynamic rheological behavior of the obtained hydrogels, and to explore the plausible mechanism for the multi-complexation between CNPs, PVA and borax for a better understanding of the relationship between 3D network structure and hydrogel properties, which could further deepen the fundamental knowledge of how hydrogels were strengthened by CNPs in the presence of borax. Insights into the structural and viscoelastic changes that occurred when the nature of CNPs were changed were obtained from analyses of rheology data. In the work, the effects of particle size, aspect ratio, crystal structure, surface charge and minimum overlap concentration of different CNPs on the dynamic rheological properties and performance of the hydrogels were investigated. Through dynamic oscillation measurements, the enhancement effect of CNPs on the composite hydrogels was verified. Since dynamic bonds formed between the $B(OH)_4^-$ and the OH groups on the sides of the PVA (and/or CNPs) are reversible and exchangeable, the self-healing ability and thermo-reversibility of composite hydrogels were also demonstrated. In addition to providing fundamental insight into factors controlling the efficiency of the cross-links and the interactions among these network components of the composite hydrogels, this work described a new type of soft matter with some unique properties that can be tuned by the incorporation of different CNPs to meet the requirements of specific applications.

2. Experimental

2.1. Materials and hydrogel preparation

Three kinds of CNPs were isolated from bleached wood pulp using alkali pretreatment and/or sulfuric acid hydrolysis followed by a high-pressure homogenization as previously described in our work (Han, Zhou, French, 2013; Han, Zhou, Wu, Liu, & Wu, 2013). The cellulose nanocrystals with I and II crystalline allomorphs as well as the cellulose nanofibers with crystal I structure were designated as CNC I, CNC II and CNF I, respectively. Their corresponding length, width and aspect ratio were 149 ± 40, 46 ± 18 and 732 ± 208 nm; 9 ± 2, 5 ± 1 and 21 ± 7 nm; 16.6, 9.4 and 36.6, respectively (Han, Zhou, Wu, et al., 2013). The obtained CNP aqueous suspensions (1.0 wt%) were stored at 5 °C in a refrigerator before use. As previously described (Han, Lei, & Wu, 2013), dried borax powder (sodium tetraborate decahydrate, over 99.5% purity, $Na_2B_4O_7 \cdot 10H_2O$, $M_w = 381.37\ \mathrm{g\,mol^{-1}}$, Aldrich Chemical Co.) was dissolved in 1.0 wt% CNP aqueous suspensions at room temperature to obtain the aqueous solutions with 0.4 wt% of borax. A weighed amount of PVA powder (2.0 wt%) ($M_w = 146{,}000–186{,}000\ \mathrm{g\,mol^{-1}}$, 99.0+% hydrolyzed, Aldrich Chemical Co.) was then gently scattered into the stirred aqueous solutions. The mixtures were stirred for 0.5 h at room temperature to prevent the PVA powder from forming lumps and to allow a complete swelling of the PVA chains. Afterwards, the solutions were heated to 90 °C and stirred for 2 h. The heating process was carried out in hermetically sealed flasks to avoid water evaporation and film formation on the surface of the solution. Once the PVA was totally dissolved, homogeneous translucent solutions with well-dispersed CNPs were obtained. The mixture began to exhibit viscoelasticity with the decreasing temperature. The solutions were further cooled to room temperature to form the final hydrogels. All the hydrogels were homogeneous and stable even after they were allowed to stand for more than 8 months at room temperature. Accordingly, the PVA-borax hydrogel was prepared by directly dissolving PVA powder (2.0 wt%) into borax aqueous solutions (0.4 wt%). All other processing conditions were the same as those used for the CNP–PVA-borax hydrogels. On the whole, all the hydrogel samples contained 2.0 wt% of PVA and 0.4 wt% of borax. The hydrogels with 1.0 wt% of CNC I, CNF I and CNC II were designated as PB-CNC I, PB-CNF I and PB-CNC II, respectively, and they were collectively referred to as CNP-reinforced PB hydrogels. The PVA-borax-water complex solution was designated as PB. Deionized water was used for the solution preparation. All solvents and reagents were of analytical grade.

2.2. Dynamic oscillation measurement

The hydrogels (PB, PB-CNC I, PB-CNF I and PB-CNC II) and suspensions (CNCI, CNF I and CNC II at 1.0 wt%) were transferred to