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Stable, self-healing hydrogels from nanofibrillated cellulose, poly(vinyl alcohol) and borax via reversible crosslinking

Steven Spoljaric, Arto Salminen, Nguyen Dang Luong, Jukka Seppälä *

Polymer Technology, Department of Biotechnology and Chemical Technology, Aalto University School of Chemical Technology, P.O. Box 16100, 00076 Aalto, Finland

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ABSTRACT

Hydrogels were prepared by blending nanofibrillated cellulose (NFC), poly(vinyl alcohol) (PVA) and borax. NFC was incorporated to alter the non-Newtonian behaviour and flow properties of the PVA–borax crosslinked system. The hybrid hydrogels maintained their shape and form under low stress, indicating enhanced material stability. Furthermore, hydrogels exhibited self-healing ability, being able to be broken apart and re-formed manually into a single continuous piece without additional external stimuli. This behaviour was attributed to the break-down and reformation of hydrogen bonds within the hydrogel. NFC fibrils contributed towards enhancing gel content and retarding swelling, essentially restricting segmental motion and water penetration. Increasing borax content had a similar effect due to closer PVA chain proximity and higher crosslink density. Compressive mechanical properties were enhanced with additions of up to 40 wt% NFC and increased borax concentrations, while creep was retarded due to the influence of NFC on flow and viscosity and greater chain restrictions via crosslinking at increased borax loadings. Both PVA:borax complexes (crosslinking) and hydrogen bonding contribute to the mechanical performance of the hydrogels. Concentrations of NFC above 40 wt% diminished structural properties, due to the nanofibrils preventing effective crosslinking and disrupting the network structure of the hydrogels.

1. Introduction

Hydrogels derived from natural polymers, including chitosan [1], starch [2], and gelatin [3], have attracted significant interest within recent years. This is partly due to growing environmental trends to switch from fossil fuel-based synthetic polymers towards macromolecules obtained from renewable and sustainable sources. However, it is their potential use in biomedical and pharmaceutical applications that is the primary drive behind this attention. Natural polymer hydrogels exhibit non-toxicity, biocompatibility, biodegradability and have the added benefit of displaying characteristics similar to soft biological tissues [4]. Within the biomedical field, these natural hydrogels show great potential as 3D-matrices for cell cultures, contact lenses, wound coverings and bandages, and selective drug release and delivery systems [4,5].

Nanocellulose derivatives have readily been utilised in hydrogel preparation [6–9], primarily to impart mechanical reinforcement into the hydrogel but also to encourage crosslinking and provide stimuli–responsive behaviour. Amongst nanocellulosic materials, nanofibrillated cellulose (NFC) is a promising choice for hydrogel material [10–13]. Aside from its abundance and renewability, NFC displays high mechanical strength and stiffness, hydrophilicity, biocompatibility, a low percolation threshold and can readily be modified to introduce functional groups or prepare cellulose derivatives. Recent hydrogels prepared

* Corresponding author. Tel.: +358 9 4702 2614; fax: +358 9 462 373.
E-mail address: jukka.seppala@aalto.fi (J. Seppälä).

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from NFC via photopolymerisation have highlighted its high water retention values and remarkable mechanical reinforcing abilities [14,15]. Co-crosslinked NFC–poly (methyl vinyl ether-*co*-maleic acid)–polyethylene glycol hydrogels Goetz et al. [16] displayed superior toughness, with optimal values achieved at NFC concentrations of 50 wt%. Dash et al. [17] enhanced the thermal stability, resistance to swelling and mechanical properties of gelatin hydrogels crosslinked with oxidised NFC. These promising results provide much opportunity to blend or compound NFC with suitable polymers and molecules, incorporating NFC's favourable intrinsic properties while tailoring hydrogel characteristics towards specific applications and environments. Additional environmental, economic and therapeutic benefit may be provided by maintaining a high-as-possible NFC concentration within the hydrogels. However, such materials may ultimately exhibit diminished or unsatisfactory properties and stability and as a result, cellulose concentrations within hydrogels have usually remained quite low [4]. Therefore, preparing high-cellulose content hybrid hydrogels with suitable compounds is an important area worth pursuing.

Poly(vinyl alcohol) (PVA) is a biocompatible, non-toxic and readily crosslinked polymer, which shows potential for blending with NFC. It is a popular choice of hydrogel material in its own right [18–21], due to its water-solubility, ability to swell and retain moisture. Despite these favourable attributes, the ease at which PVA forms hydrogels and absorbs water is often at the expense of its stability and mechanical properties [22]. Introducing a crosslinker such as borax can significantly enhance malleability, although strength and ductility remain poor. Borax readily crosslinks PVA via "di-diol" complexation as shown in Fig. 1. Although ductility and elongation is facilitated via crosslinking with borax, the PVA–borax system also displays non-Newtonian behaviour, resulting in flow under low stress and limited dimensional stability. This limitation can be overcome by blending with NFC, with the cellulose nanofibrils manipulating flow characteristics and enhancing material stability. Additionally, the interactions and entanglements that arise following NFC incorporation can be utilised to alter morphology, swelling properties, water retention ability, strength and ductility.

The few hydrogels prepared from PVA and NFC combinations have shown potential in dye-removal [23] and biomedical applications [4,24], although non-functionalised cellulose (as opposed to widely utilised carboxymethylated- or (2,2,6,6-tetramethylpiperidine-1-oxy) TEMPO-oxidised NFC) is rare due to poor solubility in normal aqueous solution [24]. Furthermore, cellulose–PVA–borax hydrogels are yet to be reported. Of the various methods available to crosslink PVA, physical crosslinking using thermal treatment provides several benefits. The procedure is effective, relatively fast and simple to perform. The method leaves no residual, harmful reagents. By controlling and manipulating crosslinking conditions, PVA hydrogels prepared via physical crosslinking have exhibited superior mechanical properties to chemical and irradiative crosslinked PVA hydrogel systems, while maintaining characteristics similar to biological tissue [20]. Finally, the possibility to prepare biocompatible hydrogels via a simple and effective method significantly increases potential applicability, usability and accessibility.

Herein, the preparation and characterisation of hydrogels derived from NFC–PVA–borax is documented. A practical and effective method of physical blending was employed to prepare the hydrogels that possessed enhanced mechanical strength, elasticity, malleability and retainment of dimensions and form. One criterion was to utilise NFC as a bulk component within the hydrogels, without compromising the properties or structural integrity of the hybrid materials. The compressive mechanical properties, chemical structure, morphology, degree of swelling and gel content of the hydrogels were characterised, with the influence of PVA:borax ratio and NFC concentration being investigated.

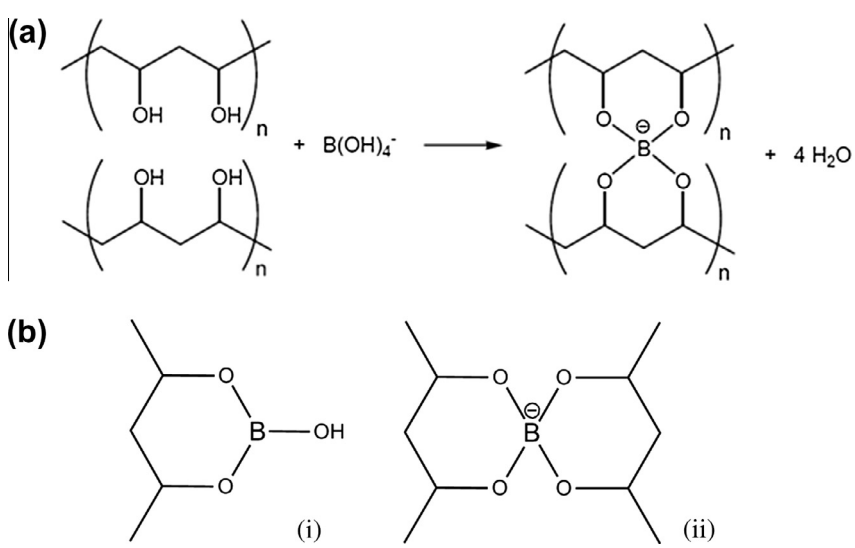

Fig. 1. (a) Crosslinking reaction between PVA and borate ions, (b) borate complexes; (i) trigonal, (ii) tetrahedral.