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

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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.

Keywords:

Nanofibrillated cellulose; hydrogel; borax; poly(vinyl alcohol); mechanical properties; self-healing material

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 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 Figure 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-oxyl) 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.

2. Experimental

2.1 *Materials*

Nanofibrillated cellulose (NFC) was provided by UPM Corporation (Helsinki, Finland), under the product name UPM Fibril Cellulose. A nominal energy consumption of $0.3 \text{ kWh}\cdot\text{kg}^{-1}$ was utilised to mechanically disintegrate bleached birch kraft pulp. The birch pulp was first pre-treated with a Masuko supermasscolloider (Masuko Sangyo Ltd., Japan) to a target SR number of 90-94. Subsequently, the material was fluidized by six passes through a M7115 fluidiser (Microfluidics Corp. Newton, MA, USA) with an operating pressure of 1,850 bar. The solids content of the prepared dispersion was 1.61 %·wt. Poly(vinyl alcohol) (Mowiol® 10-98, $M_w = 61,000 \text{ g}\cdot\text{mol}^{-1}$) and sodium tetraborate decahydrate (borax) were supplied by Sigma Aldrich, USA.

2.2 *Materials preparation*

2.2.1 Preparation of NFC-PVA-borax hydrogels

Hydrogels were prepared by crosslinking NFC and PVA with borax in solution. 5 %·wt solutions of PVA and borax were simultaneously added to the NFC dispersion and stirred for 10 min. The dispersions were kept in open petri dishes at 50 °C for 6 h. Samples were subsequently washed with isopropanol and water and then stored at 6 °C. The water content of the hydrogels were determined gravimetrically, with all hydrogels displaying water concentrations between 60-80 % of the total weight.

2.3 *Materials characterisation*

2.3.1 Attenuated total reflectance infrared spectroscopy (ATR-IR)

A Unicam Mattson 3000 FTIR spectrometer equipped with PIKE Technologies GladiATR (with diamond crystal plate) was used to characterise the chemical structure of the hydrogels, which were freeze-dried prior to analysis. All spectra were scanned within the range 400-4000 cm^{-1} , with a total of 16 scans and a resolution of 32 cm^{-1} .

2.3.2 Scanning electron microscopy (SEM)

A Zeiss SIGMA VP scanning electron microscope operating at 3 kV was used to characterise the morphology of the freeze-dried and cryo-fractured nanocomposites. Samples were mounted to the specimen holder using carbon tape.

2.3.3 Gel fraction

To determine the gel fraction of the hydrogels, pre-weighed slices were dried under vacuum at 40 °C until no change in weight was observed. Specimens were immersed in Milli-Q water for 24 h at room temperature to remove non-crosslinked species. The submerged hydrogel segments were subsequently dried at room temperature until a constant weight was achieved.

The gel fraction was calculated using Equation 1;

$$\text{Gel fraction} = \frac{W_a}{W_b} \bullet 100 \quad (1)$$

where W_a and W_b are the weights of the dried hydrogel specimens after and before rinsing/extraction, respectively. All values reported are the average of three experiments.

2.3.4 Degree of swelling

Samples were weighed and submerged in Milli-Q water at 23 °C. Specimens were periodically removed, wiped with a tissue to remove excess water and weighed. The submerged films were stored at 50 % relative humidity and all specimens were characterised in duplicate. The swelling degree was calculated using Equation 2;

$$\text{Swelling degree} = \frac{W_s - W_d}{W_d} \bullet 100 \quad (2)$$

where W_s is the weight of the film in the swollen state and W_d is the weight of the film in the dry state.

2.3.5 Static compressive analysis

Mechanical characterisation was performed using a TA Instruments Q800 Dynamic Mechanical Analyser operating in compression mode. Hydrogels were allowed to equilibrate at 30 °C for 45 min prior to mechanical testing.

2.3.5.1 Stress-strain

A force rate of 0.5 N·min⁻¹ was applied to the specimens, the experiments stopping when a maximum force of 18 N was attained. Results presented are the average of three measurements.

2.3.5.2 Creep-recovery

Creep-recovery analysis was performed by subjecting specimens to an applied stress of 0.05 MPa for 30 min, followed by a recovery period of 120 min with 0.001 MPa stress. The applied stress was chosen within the linear viscoelastic region of all hydrogels, as determined from the stress-strain data. All measurements were performed in duplicate. The four-element model of Maxwell and Kelvin-Voigt was used to interpret the creep component. The springs correspond to elastic sections with moduli E_1 and E_2 , while the dashpots represent the viscosity (η_1 , η_2). The overall deformation of the model is given in Equation 3.

$$\varepsilon(f) = (\sigma_0 / E_1) + (\sigma_0 / \eta_1) + (\sigma_0 / E_2)(1 - e^{-t/(\eta_2 / E_2)}) \quad (3)$$

The stretched exponential function of Kohlrausch, Williams and Watts (25) (KWW) was used to interpret the recovery behaviour and is given in Equation 4;

$$\phi = A \exp \left(-\left(\frac{t}{\tau} \right)^\beta \right) \quad (4)$$

where A is the pre-exponential coefficient, t is time, τ is the retardation time and β is the non-linearity coefficient ($0 < \beta < 1$). Placing the four-element model in series provides a model of

viscoelastic recovery behaviour with a distribution of relaxation times (26). Each set of springs and dashpots corresponds to a characteristic relaxation time.

3. Results and Discussion

The combination of NFC, PVA and borax produced hydrogels that were malleable, flexible and easily shaped by hand at room temperature, as shown in Figure 2. Unlike conventional crosslinked PVA-borax systems that are Maxwell solids, the NFC-PVA-borax hydrogels maintained their shape following moulding and were more viscous in behaviour. Hydrogels could be moulded into shapes that displayed structural stability and retained form. Increasing the NFC concentration enhanced shape retainment ability and form stability, though at NFC loadings of 60 %·wt the hydrogels were softer and failed to maintain shape. These initial changes in material behaviour and properties can be attributed to NFC acting as a thickening agent for the hydrogel. The cellulose-gel dispersion acts in a similar manner to an emulsion, suspending the PVA-borax system in solution and preventing water from separating out. Hydrogen bonding between NFC-NFC and NFC-PVA also occurs. Bound water within the hydrogel also plays an important role, having the potential to hydrogen bond with hydroxyl groups of NFC and PVA.

Furthermore, the incorporation of NFC within the PVA-borax system allowed the hydrogels to be broken apart and subsequently reformed into a single piece of hydrogel by hand, as shown in Figure 3 (a video of this phenomenon is available in the Additional Content). One possible explanation for this ability is attributed to the hydrogen bonds within the hydrogels. These bonds can be readily broken and reformed, allowing the hydro-gels to self-heal or 're-form'. Re-formable or self-healing hydrogels have been prepared using hydrogen bonding mechanisms (27-31), although their use is still somewhat limited. Furthermore, these hydrogels rely on heat, pH or other external stimuli to facilitate the self-healing process. The hybrid hydrogel presented here possesses a distinct advantage by exhibiting 'self-healing' or 're-formable' capabilities without the need of additional external stimuli. Zhang *et al.* (31) recently reported self-healing PVA hydrogels prepared via a freeze-thawing cycle. The ability to re-form was achieved without the need of stimuli or healing agents, citing sufficient polymer chain

mobility and free hydroxyl groups able to hydrogen bond across broken interfaces as key criteria. Although the same principles can be applied to the NFC-PVA-borax hydrogels, the added presence of cellulose nanofibrils and borax provides additional considerations (such as the influence of NFC on rheological behaviour). In order to better understand this phenomenon, stress-strain properties and the gel content were evaluated before ('pristine') and after ('re-formed') hydrogels were broken apart and subsequently re-assembled.

3.1 Attenuated total reflectance infrared spectroscopy

The spectra of the hydrogels with varying NFC concentrations are presented in Figure 4a, while the influence of PVA:borax ratio is displayed in Figure 4b. Several peaks characteristic of the hydrogels' structures are evident. A broad, large peak was observed at 3330 cm^{-1} and attributed to O-H stretching. This band correlates to hydroxyl groups that have complexed (formed crosslinks) with borate ions and those involved in intermolecular hydrogen bonding (32). The peak at 2924 cm^{-1} was attributed to C-H stretching of the CH_2 group. No visible influence on peak intensity was observed for both O-H and C-H stretching bands. Similar behaviour within PVA-chitosan-borax films was reported by Liang *et al.* (33), who determined that crosslink formation ("di-diol" complexation between borax and PVA, refer to Figure 1) may not have a distinct influence on hydrogel chemical- or hydrogen bond environment.

Hydrogels displayed several distinct peaks characteristic of the presence of borax and borate; 1423 and 1333 cm^{-1} (asymmetric stretching relaxation of B-O-C), 828 cm^{-1} (B-O stretching from residual B(OH)_4^-), 650 cm^{-1} (bending of B-O-B linkages within borate networks) (34-36). This confirms not only the occurrence of complexation/crosslinking between PVA and borate, but the presence of a borate network and small amount of B(OH)_4^- within the hydrogels. As shown in Figure 4b, increasing the PVA:borax ratio intensified peaks corresponding to B-O-B linkages within borate networks (650 cm^{-1}) while simultaneously diminishing those associated with complex formation (1423 and 1333 cm^{-1}). As the ratio between PVA:borax decreases and

approaches 3:1, the higher borate concentration increases the likelihood of crosslinking/complexation with PVA. Although hydrogels with 10:1 PVA:borax ratios exhibited peaks at 1423 and 1333 cm^{-1} , indicating crosslink formation, the bulk of the borate within these hydrogels appeared to preferentially form networks amongst themselves.

The B-O-C stretching peaks at 1423 and 1333 cm^{-1} provide further information regarding the nature of interactions between PVA and borate. Two types of complex can be formed between PVA and borate; trigonal and tetrahedral (refer Figure 1b). These correspond to the respective peaks at 1423 and 1333 cm^{-1} (37). Comparing the peak intensity of the two reveals that trigonal complexes have sharper and larger peaks and are presumably more prominent within the hydrogels than their tetrahedral counterparts. The free hydroxyl groups on trigonal complexes allow for potential hydrogen bonding with PVA and NFC and may be the dominant interaction system within the hydrogels. A proposed structure of the hydrogels, showing both crosslinking (tetrahedral complex formation) and hydrogen bonding is presented in Figure 5.

3.2 Scanning electron microscopy

Scanning electron images highlighting the influence of borax concentration on hydrogel morphology are presented in Figure 6. At a PVA:borax ratio of 3:1 (Figure 6a), a three-dimensional network morphology is evident following water removal. The voids formed following water removal are generally round in shape and exhibit a diameter of ~500-600 nm. Cellulose nanofibril aggregates are visible protruding through the network, indicating sufficient coating and interaction with the PVA. Increasing the PVA:borax ratio to 5:1 (Figure 6b) resulted in a similar morphology to its 3:1 predecessor, with negligible differences in void shape and size visible. A further increase of PVA:borax ratio to 10:1 yielded a more-open network with larger void diameters. As the crosslinking density is increased, the distance between PVA chains decreases leading to a denser, more-compact structure (38). Furthermore, hydrogel and aerogel structure is influenced by solution viscosity (39). Increasing the degree

of crosslinking increases viscosity, resulting in denser, compact materials with smaller voids. Similar observations were reported by Chen *et al.* (40) in PVA/clay gels.

Figure 7 displays the influence of NFC concentration on hydrogel morphology. When comparing concentrations of 40 (Figure 7a) and 20 %·wt (Figure 6b), a clear contrast in topography is noticeable. A denser material with smaller voids is visible, with cellulose nanofibrils extending throughout the structure. Like crosslinking, cellulose increases system viscosity via the introduction of a network structure consisting of long fibres and entanglements. Although the cellulose concentration is relatively high in relation to PVA (40 %·wt) and the fibrils are tightly packed, the extent of agglomeration is minimal. This suggests an effective dispersion of nanofibrils throughout the hydrogel, facilitated by efficient interaction and adhesion with PVA and borax species. Further addition of NFC (Figure 7b) led to sizable film-like aggregated regions and larger voids. Increasing NFC concentration leads to an increased amount of bound water within the hydrogels. The water molecules disrupt the structure of the hydrogel and act as a barrier to crosslinking. Furthermore, the high concentration of cellulose (60 %·wt) results in reduced volume for cellulose nanofibrils to disperse through, leading to increase inter-fibrillar interactions. Agglomerate formation and increased void dimension is a consequence of this behaviour.

3.3 Gel fraction and swelling degree

The gel fraction values of the hydrogels are summarised in Table 1. Highest gel fractions were observed for gels containing 20 %·wt NFC, which was expected since PVA-borax complexation had minimal interference from NFC due to its low volume. At the highest loadings of NFC (50 and 60 %·wt), the gel fraction dramatically reduced. Since the gel fraction provides an indication of crosslinking density, the data indicates that the addition of NFC at concentrations up to 40 %·wt may encourage chain entanglement and restrictions on PVA chains, creating ‘physical’ crosslinks in addition to those present via PVA-borax complexation.

However, at NFC loadings of 50 and 60 %·wt, the increased volume of nanofibrils may act as barriers to crosslink formation and disrupt the hydrogel network structure. As the borax concentration is increased, the number of potential crosslink sites increases simultaneously. Thus, hydrogels containing a PVA:borax ratio of 3:1 have greater potential to form a more numerical and denser crosslinked network than their 10:1 equivalents.

When comparing the gel content of ‘pristine’ and ‘re-formed’, at identical NFC loadings the ‘re-formed’ specimens displayed lower gel content values than their ‘pristine’ equivalents. This behaviour most likely stems from the nature of ‘de-bonding’ and ‘re-bonding’ that occurs after the hydrogels are broken apart and subsequently reformed. Figure 8 provides a summary of this phenomenon. After the hydrogels are broken into several small pieces, inter- and intramolecular hydrogen bonds (ie, bonding between NFC-NFC, NFC-PVA and interactions with trigonal borax complexes) are broken and the network structure is disrupted. Additionally, tetrahedral complexes formed between PVA-borax may also break while cellulose nanofibrils entangled throughout the PVA may be pulled out. When the gels are ‘re-formed’, several of these disrupted hydrogen bonds reform although a significant number (in addition to entanglements and tetrahedral complexes) don’t. As a result, the total number of crosslinks (both complex and entanglement ‘physical crosslinking’) as well as hydrogen bonds that contribute towards restricted chain motion are decreased, lowering the gel content. At elevated NFC concentrations (40 and 50 %·wt), the difference between ‘pristine’ and ‘re-formed’ gel content was reduced, particularly at PVA:borax ratios of 10:1. This is possibly due to the inherently low degree of crosslinking and increased water content within these systems.

The influence of PVA:borax ratio and NFC concentration on the swelling degree of the hydrogels after 48 h is summarised in Table 1, while graphical representations are presented in Figure 1 in Additional Content. Increasing the borax content reduced the degree of swelling, with all hydrogels containing PVA:borax ratios of 3:1 displaying the lowest values for their

respective NFC concentrations. As the borax concentration is increased, the likelihood of crosslink formation with PVA becomes greater. These interactions have two direct effects on swelling behaviour; Firstly, the higher proportion of interactions between PVA and borax ions reduces the total number of vacant hydroxyl groups on both molecules, slightly increasing the hydrophobic nature of the hydrogels. Subsequently, the number of vacant hydroxyl groups able to hydrogen bond with- and adsorb to water decreases. Secondly, reduced free volume and chain mobility are characteristic of crosslinked hydrogels, as the polymer chains are within closer proximity of one another at increased crosslinker concentrations. These structural restraints inhibit the ability of water molecules to penetrate, adhere and ultimately expand (swell) the hydrogel. Gel content was confirmed to increase with borax loading, as summarised in Table 1. Thus, increasing the occurrence and distribution of crosslinking decreases the corresponding network mesh size of the hydrogel (41), as confirmed by SEM (refer Figure 6).

For NFC loadings up-to and including 40 %·wt, swelling degree values decreased. Similar behaviour was reported by Chang et al. (24) within PVA-cellulose hydrogels, observing an increase in swelling degree with PVA concentration. The results suggest there is sufficient interaction between the NFC-PVA and possibly NFC-borax, hindering water adhesion and uptake while maintaining a rigid and more-compact hydrogel structure. As the cellulose concentration exceeded 40 %·wt, the degree of swelling increased reaching maximum values at 60 %·wt NFC loadings. The most probable cause of this behaviour is the large NFC volume preventing effective crosslink formation between the PVA and borax. Hydrogen bonding between NFC-PVA, NFC-trigonal borate complexes and NFC fibres can occupy hydroxyl groups that would provide potential crosslinking sites. At elevated cellulose loadings, agglomerate formation is highly likely as confirmed via SEM (Figure 7b). This disrupts the network structure of the material and creates voids throughout the hydrogel. Furthermore, the hydrophilic nature of the NFC suspension could incorporate larger quantities of water within

the hydrogels at elevated concentrations (42). Even if this water is removed via drying, the hydrogels exhibit increased free volume and less efficient chain packing than their counterparts containing NFC concentrations below 40 %·wt. This increases susceptibility to water penetration and increases the ease at which water molecules can swell and expand the hydrogels.

3.4 Mechanical analysis

3.4.1 Stress-strain

The stress-strain curves of hydrogels obtained via static compression mode are presented in Figure 9 while the data is summarised in Table 1 in Additional Content. Figure 9a displays the influence of NFC concentration, with the PVA:borax ratio maintained at 5:1. The addition of NFC had a distinct impact on the compressive modulus (E), increasing from 39.6 (20 % NFC) to 74.0 kPa (40 % NFC). Similar behaviour was exhibited by the maximum stress, with the largest values (29.0 kPa) obtained at NFC loadings of 40 %·wt. The moduli values are significantly higher than those reported by Han *et al.* (43), who reported moduli values of 0.9 kPa for pure PVA-borax hydrogels and values ranging from 3.8 to 22.5 kPa for gels reinforced with cellulose nanoparticles. This enhancement in mechanical properties can be attributed to the reinforcing influence of cellulose nanofibrils. Liu *et al.* (44) described how cellulose and PVA can form a semi-interpenetrating network. The strong interfacial interactions between the NFC and PVA impart restrictions on segments of polymer chain during deformation leading to enhanced stiffness and strength. Entangled segments of cellulose nanofibrils act as ‘physical crosslinks’, working in conjunction with borax complexes (crosslinks) towards maintaining mechanical integrity of the hydrogels. This is supported by the increased gel content observed at NFC concentrations up to and including 40 %·wt. At increased NFC loadings of 50 and 60 %·wt, both moduli and strength values decrease. A probable cause for this reduction in mechanical behaviour is the large volume of

NFC preventing effective crosslink formation between PVA and borax. Although the hydrogen bonds between NFC and PVA contribute towards the mechanical behaviour of the hydrogels, the complexation between PVA and borax are more crucial.

At a constant NFC concentration of 20 %·wt, increasing the borax concentration in the hydrogels subsequently increased the compressive modulus from 27.1 kPa (10:1) to 39.6 (5:1) and 40.5 kPa (3:1), as displayed in Figure 9b. Maximum stress exhibited similar trends to the compressive moduli, increasing from 11 (10:1) to 16 kPa (3:1). The moduli of hydrogels are primarily dependent on crosslink and charge densities (45). The enhanced strength and moduli with borax loading are attributed to the increased likelihood of crosslink formation. Hydrogels with higher borax loadings display reduced free volume and a more confined structure (refer to SEM Figure 7), leading to reduced macromolecular chain mobility resulting in stronger, tougher materials.

Since the NFC-PVA-borax hydrogels exhibited the ability to self-heal or reform following breakdown, the static compression behaviour of the ‘re-formed’ hydrogels were characterised and compared with ‘pristine’ or unbroken specimens. Test materials were pulled apart by hand into several small pieces, then hand moulded into a single piece. The stress-strain curves are presented in Figure 9c while the mechanical data is summarised in Table 2. The re-formed gels were left for 30 min prior to testing and subsequently exhibited compressive moduli values lower than their ‘pristine’ equivalents. Deforming the hydrogels results in the breaking of hydrogen bonds (NFC-NFC, NFC-PVA, trigonal borax complexes) and tetrahedral PVA:borax complexes, while also altering network structure and pulling out entangled cellulose nanofibrils. After ‘re-forming’ not all of the bonds and entanglements were reversible. Furthermore, given the thermoreversible nature of tetrahedral PVA:borax complexes (46) and that the hydrogels were ‘re-formed’ at room temperature, the likelihood of complete ‘re-complexation’ is small. The resulting ‘re-formed’ hydrogel exhibits a disrupted network

structure that differs from the original and experiences reduced restrictions on chain segmental motion during load application. Thus a decrease in modulus is observed. The stress-strain results correlate to the reduced gel content of 're-formed' hydrogels, strongly indicating that the 'de-bonding – re-bonding' mechanism is plausible.

When comparing the maximum stress values of the reformed hydrogels, a distinct trend is observed when altering the borax concentration. At lower borax loadings (PVA:borax ratio – 10:1), the maximum stress of the 're-formed' hydrogel (25.4 kPa) is higher than its 'pristine' counterpart (19.1 kPa), at a NFC concentration of 40 %·wt. This difference in strength diminishes as the PVA:borax ratio is increased to 3:1, with the 40 %·wt NFC counterpart 're-formed' hydrogel displaying a lower strength values than its 'pristine' equivalent (29.7 and 31.1 kPa, respectively). This phenomenon is consistent with other reported observations (29,47) documenting an increase in self-healing ability with reduced crosslinking density. At low degrees of crosslinking, polymer chains exhibit greater flexibility and freedom to move, increasing the possibility of bond reformation across the broken interface. The increased number of bonds provides greater strength to the hydrogels. Despite the increase in maximum stress, the moduli of the 're-formed' hydrogels continued to display lower values than their 'pristine' counterparts. Therefore, the modulus appears to be dependent on tetrahedral PVA:borax complexes(crosslinks) while material strength is governed by intermolecular hydrogen bonding. The reinforcing- and viscosity-modifying ability of NFC appears to influence both modulus and strength, as observed by identical trends in values for both 're-formed' and 'pristine' hydrogels as a function of NFC concentration.. The stress-strain data indicates that optimal mechanical properties were achieved using a NFC concentration of 40 %·wt.

3.4.2 Creep-recovery

As shown in Figure 10a, increasing NFC concentration reduced creep within the hydrogels. Due to the complex nature of the PVA-NFC-borax systems, it's likely that several inter-related factors contribute towards creep behaviour. Firstly, as observed during stress-strain analysis, increasing the NFC concentration enhanced strength and moduli values up to and including 40 %·wt, therefore acting as reinforcement. However, maximum reinforcement values were obtained at loadings of 40 %·wt, and hydrogels containing 50 and 60 %·wt NFC were less-stiff and softer. Thus, the reduction in creep cannot be attributed solely to NFC's reinforcing ability. The second, closely-related factor stems from NFC's ability to modify flow and rheological properties. Pure PVA-borax hydrogels are non-Newtonian in nature, meaning they will flow under low stress. Indeed, this is observed during the relaxation segment, with strain continuing to increase with time. The non-Newtonian behaviour decreases with increasing NFC concentration, as the cellulose fibrils cause chain entanglements amongst PVA. The incorporation of large molecular weight species, such as NFC (48) increase hydrogel viscosity and essentially thicken the system. This increased thickness also leads to the third factor involved in creep retardation; reduced water flow/seepage during load application. The NFC-gel dispersion behaves in a similar manner to an emulsion, suspending the PVA-borax system in solution and preventing water from separating out. Hunt (49) and Wong (50) similarly observed a correlation between reduced creep and water expulsion for PVA-hydrogel systems. The incorporation of cellulose nanofibrils into PVA-borax hydrogels can potentially restrict the rate of water expulsion under load, contributing towards the creep resistance of the hydrogels. As anticipated, increasing the PVA:borax ratio (Figure 10b) helped retard creep due to an increased likelihood of crosslinking and stiffer, tougher nature of the hydrogels.

The parameters of the four-element model were calculated for the selected hydrogels, with the results being summarised in Table 2. The hydrogel containing 20 %·wt NFC displayed a Maxwell modulus (E_1) value of 0.028 MPa. The addition of NFC increased E_1 , reaching a maximum of 0.097 MPa at loadings of 40 %·wt. Higher cellulose concentrations caused E_1

values to diminish. Since E_1 corresponds to the elastic modulus, the increased values are indicative of the limited reinforcing ability of NFC and suggest an increase in stiffness. Similarly, an increase in Maxwell viscosity (η_1) with NFC loading was observed, confirming that cellulose nanofibrils contribute towards deformation resistance. Both E_1 and η_1 increased as the PVA:borax ratio became closer, indicative of greater restrictions on chain motion and flow induced by greater crosslinking. All hydrogels displayed permanent deformation, which is characteristic of viscoelastic materials. Increasing the NFC concentration reduced permanent deformation, as the viscosity and flow properties of the hydrogels were altered. The increase in Voigt viscosity (η_2) with NFC concentration further suggests that flow restrictions were imparted by the cellulose nanofibrils and resistance to PVA chain uncoiling was provided. Although hydrogels with PVA:borax ratios of 3:1 and 5:1 displayed similar permanent deformation values, a clearer comparison is observed with 10:1 loadings. The increased permanent deformation with added borax loading is due to crosslinks restricting the relaxation of PVA chains, increasing irreversible chain slippage and obstructing random coil reformation. The retardation time (τ) is the time required for the Voigt element to recover to 63.21 % (or $1 - 1/e$) of its total deformation. The addition of NFC up to 40 %·wt reduced τ values, while higher loadings increased the retardation time. The initial decrease in τ suggests that the hydrogels become more solid-like in behaviour, stemming from the limited reinforcing ability of NFC. Similarly, decreasing borax content within the hydrogels reduced the retardation time, as looser macromolecule chain configuration results in a greater degree of chain mobility and subsequent rearrangement.

To further analyse the recovery behaviour of the hydrogels, the KWW stretched exponential function was applied, as displayed in Equation 4. The results are summarised in Table 3. Both the pre-exponential factor (A) and the shape fitting parameter (β) changed with NFC and borax concentration. Various factors influence the value of β , including material structure,

crosslinking, crystallinity and the presence of fillers or other additives. These observations strongly indicate the influence of NFC loading and the degree of crosslinking on flow restriction of PVA chains. The relaxation time gives an estimate of the degree of mobility molecules within the polymer matrix possess. As with the retardation time (τ), the relaxation time reached a minimum at 40 %·wt before increasing at higher NFC concentrations. This suggests that the hydrogels are ‘most solid-like’ at NFC loadings of ~40 %·wt. The model data obtained from the 4-element model and KWW function are in good correlation with experimental creep-recovery and stress-strain data.

4. Conclusion

Physical blending was utilised to prepare hydrogels from nanofibrillated cellulose (NFC), poly (vinyl alcohol) (PVA) and borax. The usual non-Newtonian nature of pure PVA-borax systems was altered by the incorporation of NFC, with the hybrid hydrogels retaining their shape and form. This stability was retained after the gels were hand-moulded into new shapes and structures. Hydrogels also displayed self-healing properties, being able to be ‘re-formed’ into a single, continuous piece after being broken into several pieces without the need for additional external stimuli. This behaviour stems from the ability of NFC to alter hydrogel viscosity and the ‘de-bonding – re-bonding’ of hydrogen bonds. Increasing the borax concentration resulted in a more-compact morphology, as PVA chains were in closer proximity to one another. NFC addition resulted in a more-compact network structure at loadings up to 40 %·wt due to increased system viscosity, while higher concentrations disrupted the structure via increased water content. Gel content increased while swelling decreased with elevated NFC content, reaching a limit at concentrations of 40 %·wt. This was attributed to the nanofibrils restricting PVA chain motion and retarding water penetration. Larger NFC loadings diminished properties, due to a disrupted network structure. ‘Re-formed’ hydrogels displayed lower gel content values than their ‘pristine’ counterparts, due to altered hydrogel structure and irreversible bond/complex/entanglement recovery following reformation. The greater likelihood of crosslink formation and more-restricted structure at higher borax loadings resulted in larger gel content and reduced swelling values.

Moduli and strength values reached maximum limits at NFC concentrations of 40 %·wt, with the nanofibrils restricting segmental motion during deformation. Mechanical properties diminished at higher NFC loadings due to the increased volume of fibres hindering crosslink formation. ‘Re-formed’ hydrogels displayed slightly lower moduli and strength values than their ‘pristine’ equivalents due to the aforementioned ‘de-bonding – re-bonding’ mechanism. Increasing the borax concentration created a more restricted network structure, enhancing

stress-strain properties while reducing creep. NFC retarded creep by altering the flow properties during load application. The four-element model and KWW function were in good correlation with the experimental data. The self-healing and moulding abilities of the hydrogels, in conjunction with its morphology and related properties, display great potential for applications including wound and bandage coverings or filters/adsorbents for various molecules. However, it must be emphasised that given the moisture and pH sensitivity of PVA-crosslinked systems, rigorous analysis of the interactions with biological systems must be performed to ensure hydrogel degradation and borate complexation with molecules in biological solutions does not occur.

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List of Tables and Figures

Tables:

Table 1: Gel fraction and swelling degree data of hydrogels

Material		Gel content (%)		Degree of swelling after 48 h (%)
<i>PVA:borax ratio</i>	<i>NFC concentration (%·wt)</i>	<i>‘Pristine’</i>	<i>‘Re-formed’</i>	
3:1	20	70.6 ± 3.2	67 ± 2.5	256.1 ± 8.2
3:1	30	65.8 ± 2.6	60 ± 2.8	235.7 ± 5.7
3:1	40	55.0 ± 4.5	48 ± 3.3	226.1 ± 5.6
3:1	50	25.4 ± 3.1	23 ± 2.6	327.4 ± 11.8
3:1	60	18.5 ± 2.0	18 ± 1.8	453.7 ± 9.3
5:1	20	67.4 ± 2.4	64 ± 1.0	302.4 ± 7.2
5:1	30	60.1 ± 4.9	58 ± 2.4	287.6 ± 5.0
5:1	40	52.3 ± 3.1	45 ± 4.7	275.8 ± 6.8
5:1	50	21.7 ± 3.7	20 ± 3.1	457.6 ± 9.7
5:1	60	15.2 ± 4.2	14 ± 2.8	612.8 ± 8.5
10:1	20	62.6 ± 4.0	61 ± 3.1	668.8 ± 7.7
10:1	30	55.5 ± 2.0	52 ± 3.9	634.8 ± 5.6
10:1	40	47.6 ± 3.5	45 ± 4.6	602.5 ± 8.4
10:1	50	20.4 ± 3.3	20 ± 2.7	807.9 ± 6.9
10:1	60	13.4 ± 4.7	13 ± 3.0	1102.4 ± 8.1

Table 2: Creep-recovery data of selected hydrogels

PVA:borax ratio	NFC conc. (%·wt)	E₁ (kPa)	η₁ (MPa·s⁻¹)	E₂ (kPa)	η₂ (kPa·s⁻¹)	τ (min)	Permanent deformation (%)
5:1	20	28.0	110.0	4.9	39.0	7.95	109
5:1	30	76.0	117.7	7.8	44.7	5.69	107
5:1	40	96.6	120.0	12.8	59.9	4.68	90
5:1	50	68.9	122.6	14.3	96.4	6.72	85
5:1	60	29.0	125.3	18.3	170.9	9.34	85
3:1	50	92.2	126.4	17.1	192.2	11.25	85
5:1	50	68.9	122.6	14.3	96.4	6.72	85
10:1	50	56.8	120.7	12.8	58.8	5.50	80

Table 3: KWW parameters of selected hydrogels

PVA:borax ratio	NFC conc. (%·wt)	A	β	τ (s)
5:1	20	153.0	-0.12	32.35
5:1	30	84.10	-0.01	23.07
5:1	40	102.50	0.01	22.71
5:1	50	79.22	0.03	26.78
5:1	60	55.20	0.04	28.01
3:1	50	60.00	0.07	20.84
5:1	50	79.22	0.03	26.78
10:1	50	98.43	0.01	33.72

Figures:

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

Fig. 2: Shape-retainment and dimensional stability of NFC-PVA-borax hydrogels at 23 °C: a) pure PVA-borax hydrogel (5:1 ratio), b) flow after 5 min, c) stable NFC-PVA-borax hydrogel (PVA:borax ratio = 5:1, NFC concentration 50 %·wt) retaining their shape and form, after 25 min

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Fig. 4: ATR-FTIR spectra of hydrogels displaying the influence of; a) NFC concentration (PVA:borax ratio for all spectra: 5:1), b) PVA:borax ratio (NFC concentration for all spectra: 40 %). The peaks attributed to B-O-C stretching are highlighted

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Fig. 6: Scanning electron microscope images of the influence of PVA:borax ratio on hydrogel morphology (NFC concentration in all hydrogels 20 %); a) 3:1, b) 5:1, c) 10:1. Samples were freeze-dried prior to imaging.

a)

b)

c)

Fig. 7: Scanning electron microscope images of the influence of NFC concentration on hydrogel morphology (PVA:borax ratio in all hydrogels 5:1); a) 40 % NFC, b) 60 %NFC. Samples were freeze-dried prior to imaging.

a)

b)

Fig. 8: ‘De-form – re-form’ mechanism of the NFC-PVA borax hydrogels (red lines denote NFC while green lines represent PVA). Following deformation, hydrogen bonds, complexes and entanglements are broken. After the hydrogel is moulded into a single piece, several interactions may be reformed, although several are also lost

Fig. 9: Stress-strain curves of hydrogels displaying the influence of; a) NFC concentration (PVA:borax ratio for all spectra: 5:1), b) PVA:borax ratio (NFC concentration for all spectra: 20 %), c) curves of ‘pristine’ (solid lines) and ‘re-formed’ (dotted lines) hydrogels (NFC concentration for all spectra: 30 %)

Fig. 10: Creep-recovery curves of hydrogels displaying the influence of; a) NFC concentration (PVA:borax ratio for all spectra: 5:1), b) PVA:borax ratio (NFC concentration for all spectra: 40 %)

Additional content:

Table 1: Stress-strain data of hydrogels

Material		Compressive modulus (kPa)		Maximum stress (kPa)	
<i>PVA:borax ratio</i>	<i>NFC concentration (%wt)</i>	<i>'Pristine'</i>	<i>'Re-formed'</i>	<i>'Pristine'</i>	<i>'Re-formed'</i>
3:1	20	40.5 ± 2.7	37.6 ± 3.2	16.0 ± 2.5	14.9 ± 2.6
3:1	30	58.1 ± 3.5	45.0 ± 1.8	31.2 ± 1.9	30.6 ± 1.7
3:1	40	81.5 ± 0.9	70.8 ± 2.6	31.1 ± 2.4	29.7 ± 2.5
3:1	50	47.0 ± 1.4	32.1 ± 3.0	14.7 ± 0.7	11.9 ± 3.4
3:1	60	40.0 ± 3.2	32.8 ± 2.5	13.3 ± 2.5	13.7 ± 2.4
5:1	20	39.6 ± 3.2	31.9 ± 2.9	14.4 ± 3.5	16.1 ± 2.3
5:1	30	56.3 ± 3.0	34.7 ± 1.7	19.1 ± 2.8	22.9 ± 2.7
5:1	40	74.0 ± 2.8	66.4 ± 2.5	29.0 ± 1.3	30.3 ± 1.8
5:1	50	43.5 ± 2.4	35.4 ± 3.0	14.6 ± 2.7	14.5 ± 2.6
5:1	60	27.5 ± 4.0	30.1 ± 2.6	12.1 ± 0.6	14.2 ± 1.5
10:1	20	27.1 ± 2.1	25.1 ± 2.3	11.0 ± 2.6	13.8 ± 3.5
10:1	30	33.0 ± 1.9	28.6 ± 1.9	17.0 ± 1.8	20.7 ± 2.4
10:1	40	66.0 ± 4.5	60.8 ± 3.2	19.1 ± 2.4	25.4 ± 1.7
10:1	50	45.2 ± 3.8	44.8 ± 4.4	13.7 ± 3.5	13.7 ± 2.8
10:1	60	28.1 ± 3.7	30.7 ± 3.8	12.5 ± 1.2	13.1 ± 2.6

Fig. 1: Swelling degree as function of immersion time of selected hydrogels, displaying the influence of; a) PVA:borax ratio (NFC concentration for all spectra: 40 %), b) NFC concentration (PVA:borax ratio for all spectra: 3:1)