



The effects of morpholine pre-treated and carboxymethylated cellulose nanofibrils on the properties of alginate-based hydrogels

Amaka J. Onyianta^{a,*}, Maila Castellano^b, Mark Dorris^a, Rhodri L. Williams^a, Silvia Vicini^{b,*}

^a Material Chemistry and Processing, School of Engineering and Built Environment, Edinburgh Napier University, Edinburgh, EH10 5DT, United Kingdom

^b Department of Chemistry and Industrial Chemistry, University of Genoa, Genoa, 16146, Italy

ARTICLE INFO

Keywords:

Hydrogels
Alginates
Cellulose nanofibrils (CNF)
Carboxymethylation
Surface modification
Compressive modulus

ABSTRACT

The effects of varying percentage loadings of morpholine pre-treated cellulose nanofibrils (MCNF) and carboxymethylated cellulose nanofibrils (CMCNF) on the aqueous swelling, compressive modulus and viscoelastic properties of calcium-ion-crosslinked alginate hydrogels were investigated. In addition, the pore structures of hydrogels with the highest compressive modulus were studied. The incorporation of 5 wt. % MCNF resulted in a slightly reduced aqueous swelling, a 36% increase in compressive modulus and a layered pore structure when compared with the neat alginate hydrogel. On the other hand, the addition of CMCNF at the same loading led to a slightly improved aqueous swelling, an increase in compressive modulus (17%) and high porosity. Further increases in CNF loadings did not result in significant increase in material properties. The alginate/CNF composite materials have potentials to be used in applications where good swelling and mechanical robustness are required.

1. Introduction

Polysaccharidic biopolymers such as alginates, cellulose, chitosan, chondroitin sulphate and hyaluronic acid are widely researched for applications in biomedical (Aravamudhan, Ramos, Nada, & Kumbar, 2014), pharmaceutical/drug delivery (Cardoso, Costa, & Mano, 2016), packaging (Hubbe, Ferrer, Tyagi, Yin, & Salas, 2017), and agricultural fields (Guilherme et al., 2015). These materials provide potentials for low cost and sustainable products because of their ubiquitous sources of extraction. Moreover, their inherent non-toxic, biocompatible and biodegradable properties have made them well recommended in biomedical applications for bone and tissue regeneration (Park et al., 2017), wound care dressings (Leppiniemi et al., 2017) and for the delivery of various drugs and growth factors (Aravamudhan et al., 2014; Augst, Kong, & Mooney, 2006).

Naturally occurring in seaweed and brown algae, Sodium Alginate (SA) is a linear unbranched polymer consisting of β -D-mannuronic acid (M) and α -L-guluronic acid (G) arranged in a chain sequence of MM-GG-MG (Augst et al., 2006). The presence of carboxyl groups on the surface of SA promotes hydrophilicity and solubility in water. These carboxyl groups can also engage in ionic crosslinking with divalent ions such as Ca^{2+} and Ba^{2+} in the well-known “egg-box” model to form relatively stable network structures. The properties of the resulting network structure are influenced by the type of crosslinking ions, concentration

of crosslinking ions, temperature, time and method of gelation (Kuo & Ma, 2001; Vicini, Mauri, Wichert, & Castellano, 2017).

Calcium ions are mostly used for the ionic crosslinking of SA. These ions have been introduced internally within the SA solution from a slurry of CaCO_3 -D-glucono- δ -lactone system (Kuo & Ma, 2001), diffused from internally dispersed Ca^{2+} enriched microbeads (Vicini, Castellano, Mauri, & Marsano, 2015; Vicini et al., 2017), diffused from a bath of CaCl_2 solution (Ma et al., 2017) or sprayed onto the SA solution (Lin et al., 2014). The internal gelation method for SA crosslinking has been noted to provide more controlled gelation compared to the external gelation/diffusion method, which usually results in a spontaneous and heterogeneous material, characterised by a hard outer shell and a soft inner core (Kuo & Ma, 2001). To reduce the rate of diffusion and gelation, Bajpai, Shukla, and Bajpai, 2016 added SA solution to 8 kDa molecular weight cut off filtration membrane, before crosslinking in a bath of CaCl_2 . The study shows that the gelation process started from the outer circumference of the SA solution before gradually diffusing into the inner core. However, the homogeneity of the resulting hydrogel prepared using this method was not investigated.

Regardless of the gelation method used for the crosslinking of sodium alginate, the use of lower concentration of crosslinking ions leads to a material with high moisture absorbance and low mechanical properties. Increasing the concentration of the crosslinking ions however result to a material with low swelling and high mechanical properties (Augst et al.,

* Corresponding authors.

E-mail addresses: a.onyianta@napier.ac.uk (A.J. Onyianta), silvia.vicini@unige.it (S. Vicini).

2006). High mechanical and good swelling properties are desirable properties in the fields of biomedicine. In order to achieve the properties that would be fit for specific applications, many studies have focused on formulating blends of alginate with synthetic and natural polymers (Kong & Mooney, 2003; Lee et al., 2004; Lin et al., 2014). These alginate-based composites can be formulated in the form of films, sponges and hydrogels (Augst et al., 2006). Being a three-dimensional network material, hydrogels are capable of absorbing large amount of solvent without dissolving and are therefore topical materials for various biomedical applications (Ahmed, 2015).

Nanocellulose is a nano-sized cellulose material extracted in the form of rod-like crystals (cellulose nanocrystals, CNC) and nanofibrils (cellulose nanofibrils, CNF) using various chemical (Onyianta, Dorris, & Williams, 2018), enzymatic (Beyene et al., 2017) and mechanical pre-treatments followed by mechanical processing (Abdul Khalil et al., 2014). It is a renewable, biocompatible and biodegradable biopolymer with improved mechanical strength, lightweight properties, optical properties, barrier properties and structuring capabilities (Jonoobi et al., 2015; Klemm et al., 2011). Hence, the increased industrial and research interests on nanocellulose for wide range of applications. Some of the chemical pre-treatment methods such as carboxymethylation (Wågberg et al., 2008), 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-mediated oxidation (Isogai, Saito, & Fukuzumi, 2011), and quaternisation (Aulin, Johansson, Wågberg, & Lindström, 2010) modify the surface of the cellulose, thereby imparting new properties which are different from the original cellulose material. Onyianta et al. (2018) compared the properties of cellulose nanofibrils prepared using three types of chemical pre-treatment methods. The study shows that the presence or absence of surface charge on the CNF is responsible for the changes in crystallinity, viscoelasticity, thermal properties and aspect ratios of these CNF materials.

Interest in SA/nanocellulose blends in particular has increased, mainly because of the reinforcing capability of nanocellulose (Huq et al., 2017; Lin et al., 2014; Ma et al., 2017; Smyth et al., 2018). These blends of SA and nanocellulose are mostly prepared by external gelation method, which is a fast gelling method with possible areas of localised gelation. In addition, the carboxyl groups on the TEMPO-oxidised nanocellulose has been reported to participate in the crosslinking process with Ca^{2+} ions (Lin, Bruzzese, & Dufresne, 2012). However, studies on how the presence or absence of surface charge of the CNF and varying amounts of CNF affect the elastically effective crosslinking chains of SA hydrogel are still lacking.

In this study, slower diffusion and homogeneous crosslinking of SA hydrogels were prepared using calcium chloride enriched agar wells, a method adapted from Stagnaro, Schizzi, Utzeri, Marsano, and Castellano, 2018. The effect of temperature and duration of crosslinking on the homogeneity of the neat alginate hydrogels were initially studied. Subsequently, the effects of unmodified and surface modified cellulose nanofibrils on the surface interaction, equilibrium swelling, storage modulus, compressive modulus and morphology of alginate hydrogels were investigated. The modified Flory's equation (Flory, 1953) for the deformation of a swollen polymer network, based on the affine network model was then used to calculate the effect of the two types of CNF on the elastically effective chains of SA hydrogels at varying loadings. The affine network model assumes that macromolecular deformation of a network structure directly translates to the deformation of the elastically effective chains within the structure. This model has been used to characterise the elastically effective crosslinking degree of other hydrogel materials from natural and synthetic origins (Muniz & Geuskens, 2001; Sannino et al., 2005).

2. Experimental

2.1. Materials

Medium viscosity SA from brown algae, with molecular weight

ranging from 80,000 to 120,000 g/mol and composed of approximately 61% mannuronic and 39% guluronic acids (M/G ratio of 1.56), calcium chloride (CaCl_2) and sodium chloride (NaCl) were used as received from Sigma-Aldrich. Agar powder by BD Difco™ was used for the gel moulds. Two types of aqueous CNF suspensions (1 wt. %) were used to prepare SA_CNF dispersions at different loadings relative to the amount of SA solid content. The first CNF was produced using aqueous morpholine pre-treatment before the mechanical processing (MCNF) and has negligible surface charge. The second CNF was prepared by carboxymethylation pre-treatment before the mechanical processing (CMCNF) and has 550 $\mu\text{mol/g}$ of anionic carboxymethyl groups on its surface. The details and material properties of the two types of CNF used in this study are well described previously by Onyianta et al. (2018). Deionised water was used throughout the experiment.

2.2. Preparation of SA solution and SA_CNF dispersions

2 wt. % SA solution was prepared as a control by dissolving the appropriate amount of SA powder in water under continuous stirring for not less than 2 h using a magnetic stirrer. 100 g SA_CNF dispersions were prepared by weighing out appropriate amounts of CNF suspension into a beaker and diluted with the required amount of water and stirred. A constant mass of 2 g SA powder was then added to the diluted CNF suspension to make 2 wt. % SA having 5, 10 and 20 wt. % MCNF or CMCNF relative to the dry mass of SA, designated as SA_MCNF_5, SA_MCNF_10, SA_MCNF_20, SA_CMCNF_5, SA_CMCNF_10 and SA_CMCNF_20. The increment in CNF loading was by multiples of 2.

2.3. Preparation of agar gel moulds and SA_CNF hydrogels

Agar powder was added to 0.5 M CaCl_2 solution at 1 wt. % and brought to boil to dissolve the agar. 15 g of the solution was weighed into small 55 x 15 mm petri-dishes and allowed to gel at room temperature for not less than 2 h. After complete gelation of the agar solution, cylindrical glasscutter with 28 mm internal diameter was used to create wells within the agar gels. 4.5 g of SA solution or SA_CNF dispersions were then added into the wells created within the agar gels. A rectangular glass slab was gently placed on top of the SA solution to prevent bulging of the gels during crosslinking and to maintain the cylindrical shape of the hydrogels. At the end of the crosslinking process, which was visually assessed by a change from translucent light brownish colour to opaque light brownish colour, the gels were thoroughly washed in deionised water and swollen to an equilibrium state.

2.4. Equilibrium swelling of the never-dried hydrogels in water

The never-dried hydrogels were swollen in water to an equilibrium point, with the aim of characterising the network structure of the hydrogels. The mass of the equilibrium swollen hydrogel and the oven dried mass were recorded and used for the calculation of the swelling degree using the relationship given in Eq. (1).

$$\text{Swelling degree} = \left(\frac{W_s - W_d}{W_d} \right) \quad (1)$$

Here, W_d is the dry mass of the hydrogel and W_s is the swollen mass of the hydrogel.

2.5. Homogeneity test

A facile homogeneity test (Kuo & Ma, 2001) was initially carried out on the equilibrium swollen neat SA hydrogels to study the effect of the crosslinking temperature and duration on the uniformity of the crosslinks formed within the hydrogels. The tests were carried out at 4 °C, 25 °C and 37 °C for 24 h, 48 h and 72 h. Since the crosslinking process occurred by diffusion of the calcium ions from the agar gel into the SA

Download English Version:

<https://daneshyari.com/en/article/7781447>

Download Persian Version:

<https://daneshyari.com/article/7781447>

[Daneshyari.com](https://daneshyari.com)