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Ice templated and cross-linked xylan/nanocrystalline cellulose hydrogels

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ABSTRACT

Structured xylan-based hydrogels, reinforced with cellulose nanocrystals (CNCs), have successfully been prepared from water suspensions by cross-linking during freeze-casting. In order to induce cross-linking during the solidification/sublimation operation, xylan was first oxidized using sodium periodate to introduce dialdehydes. The oxidized xylan was then mixed with CNCs after which the suspension was frozen unidirectionally in order to control the ice crystal formation and by that the pore morphology of the material. Finally the ice crystal templates were removed by freeze-drying. During the freeze-casting process hemiacetal bonds are formed between the aldehyde groups and hydroxyl groups, either on other xylan molecules or on CNCs, which cross-links the system. The proposed cross-linking reaction was confirmed by using cross-polarization magic angle spinning (CP/MAS) nuclear magnetic resonance (NMR) spectroscopy. The pore morphology of the obtained materials was analyzed by scanning electron microscopy (SEM). The materials were also tested for compressive strength properties, both in dry and water swollen state. All together this study describes a novel combined freeze-casting/cross-linking process which enables fabrication of nanoreinforced biopolymer-based hydrogels with controlled porosity and 3-D architecture.

1. Introduction

Hydrogels are physically and/or chemically cross-linked polymer networks that are able to absorb large amounts of water. There are numerous applications for hydrogels, especially in the medical and pharmaceutical industry due to their excellent biocompatibility, soft tissue consistency resemblance and permeability to metabolites and oxygen (Peppas, Bures, Leobandung, & Ichikawa, 2000; Peppas, Hilt, Khademhosseini, & Langer, 2006). Along with a wide range of synthetic polymers, various biopolymers have been investigated for hydrogel formulations, typically hyaluronic acid, chitosan, cellulose and starch derivatives, alginate, dextran, collagen, and gelatin (Van Vlierberghe, Dubruel, & Schacht, 2011). Polysaccharides have a number of advantages over synthetic polymers as hydrogel components since they usually are abundant, renewable, biocompatible, biodegradable, non-toxic, and may have unique properties that cannot be easily mimicked through chemical synthesis (Coviello, Matricardi, Marianecci, & Alhaique, 2007). In the current trend for a more effective utilization of biomass (Ragauskas et al., 2006), hemicelluloses have emerged as a new potential group of polysaccharides in the development of new materials. Even though hemicelluloses, such as xylans, mannans and xyloglucans, are known to have gelling and film forming properties appropriate for production of biodegradable hydrogels (cf. Ebringerová, Hromáková, Heinze, 2005), relatively few examples of hemicelluloses-based hydrogels have been reported in the literature (Lindblad, Sjöberg, Albertsson, & Hartman, 2007). However, during the last couple of years the emerging interest in research on advanced materials based on renewable biopolymer resources have resulted in a number of publications which clearly demonstrates the potential of using xylan in hydrogel formulations (e.g. Chimphango, van Zyl, & Görgens, 2012; Karaaslan, Tshabalala, Yelle, & Buschle-Diller, 2011; Meena, Lehnen, Schmitt, & Saake, 2011; Peng, Ren, Zhong, Peng, & Sun, 2011; Pohjanlehto, Setälä, Kammiovirta, & Harlin, 2011; Silva, Habibi, Colodette, & Lucia, 2011).

Xylans are the most common hemicelluloses, and constitute 25–35% of the dry biomass of woody tissues of dicots and lignified tissues of monocots and occur up to 50% in some tissues of cereal grains (Ebringerová & Heinze, 2000). In terrestrial plants, xylans are heteropolymers, possessing a linear

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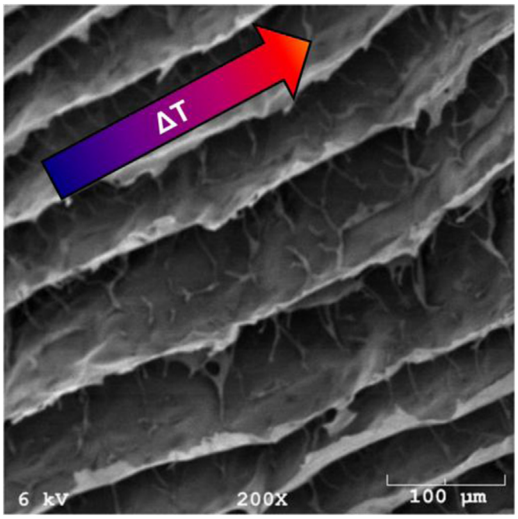

Fig. 1. SEM image of a freeze-cast xylan–cellulose nanocrystal composite foam cross-section. The lamellar structure is aligned with the temperature gradient imposed during the solidification process.

β-(1→4)-D-xylopyranan backbone substituted with a number of different side chains/groups, where L-arabinofuranosyl and 4-*O*-methyl-D-glucopyranosyl uronic acid units are most common. The great abundance of xylan in nature, along with the fact that xylans are readily available in residues and side-streams in the forestry/pulp and agricultural industry, makes xylans highly attractive as biopolymer resources in the development of new green materials (Hansen & Plackett, 2008). Furthermore, the xylan backbone has an affinity to cellulose and will adsorb irreversibly on cellulosic surfaces, a propensity that provides great opportunities for the use of xylans in cellulose-based composites (Köhnke, Brelid, & Westman, 2009; Köhnke, Lund, Brelid, & Westman, 2010; Köhnke, Östlund, & Brelid, 2011).

We have recently reported that highly structured biofoams can be prepared from xylan and cellulose nanocrystal (CNC) suspensions by employing an ice-templating technique (Köhnke, Lin, Elder, Theliander, & Ragauskas, 2012; Köhnke, Theliander, & Ragauskas, 2012). The ice-templating technique, also known as freeze-casting, involves freezing of an aqueous suspension followed by sublimation of the solidified phase under reduced pressure (cf. Deville, 2008; Gutiérrez, Ferrer, & del Monte, 2008; Wegst, Schecter, Donius, & Hunger, 2010). During the freezing operation, xylan molecules and CNCs are rejected from the moving solidification front, concentrated and finally entrapped between the growing solvent crystals. Consequently, this ice-segregation-induced self-assembly process yields materials with porous structures where the pores are a replica of the ice crystals. By employing unidirectional solidification we were able to design low density xylan biofoams which possessed a lamellar structure (Fig. 1), a porosity of 92–95% and a very high degree of pore interconnectivity (>99%) (Köhnke, Lin, et al., 2012; Köhnke, Theliander, et al., 2012).

If these biofoams could be stabilized by cross-linking, the applied freeze-casting process would enable fabrication of polysaccharide based hydrogels with controlled porosity and 3-D architecture. It is widely accepted that aldehyde groups in polysaccharides react with nearby hydroxyl groups to form intra- and inter-chain hemiacetals (cf. Kristiansen, Potthast, & Christensen, 2010). The formation of these bonds is known to influence oxidation reactions (Painter & Larsen, 1970), induce aggregation (Maia, Carvalho, Coelho, Simões, & Gil, 2011) or even gelation (Christensen, Aasprong, & Stokke, 2001). It has recently been reported that micro fibrillated cellulose containing aldehyde groups may form hemiacetal bonds during freeze-drying (Brodin & Theliander, 2012), which increases the water wet integrity of the material in analogy with aldehyde containing wet-strength resins in papermaking (cf. Chen, Hu, & Pelton, 2002; Saito & Isogai, 2006). In this study we want to investigate if this cross-linking approach could be used to stabilize our freeze-cast nanoreinforced xylan-based biofoams and by that increase the wet integrity of the material. An important consequence of unidirectional solidification is the ice-segregation-induced self-assembly. This will concentrate the oxidized xylan polymers, bringing the molecules into closer contact, which would promote the formation of cross-linking hemiacetal bonds.

The investigated procedure to form xylan–cellulose nanocrystal composite hydrogels, including the proposed cross-linking mechanism, is presented in Fig. 2. Xylan is first oxidized using sodium periodate to introduce dialdehydes. The oxidized xylan is then mixed with CNCs, frozen and freeze-dried. During the freeze-casting process hemiacetal bonds are formed between the aldehyde groups and hydroxyl groups, either on other xylan molecules or on CNCs, which cross-links the system. This combined freeze-casting/cross-linking process would enable the fabrication of polysaccharide based hydrogels with controlled porosity and 3-D architecture.

2. Experimental

2.1. Material

Oat spelt glucuronoarabinoxylan (GAX) was obtained from Sigma–Aldrich. This xylan fraction has been reported to contain 81% xylose, 9.8% arabinose, 7.6% glucose, 1.4% galactose and 0.2% of mannose (Saxena & Ragauskas, 2009).

2.2. Oxidation of xylan

Introduction of aldehyde groups to xylan was performed by oxidation using sodium periodate. A solution of GAX was prepared by heating a mixture of 5.00 g GAX and 100 mL deionized water to boiling under stirring. The solution was then cooled to room temperature, after which a specific amount of $NaIO_4$ (1.00, 3.00, 5.00 mmol/g GAX), dissolved in 100 mL deionized water, was added. The solution was stirred for 24 h in the absence of light at room temperature. The product was then purified by dialysis (Spectra Por 2, MWCO: 12–14 kDa) against deionized water. One part of the oxidized GAX was reduced with sodium borohydride. The pH of 40 mL oxidized dialyzed xylan solution was increased to 8 by addition of a few drops of 0.1 M NaOH, after which 0.5 g $NaBH_4$ was

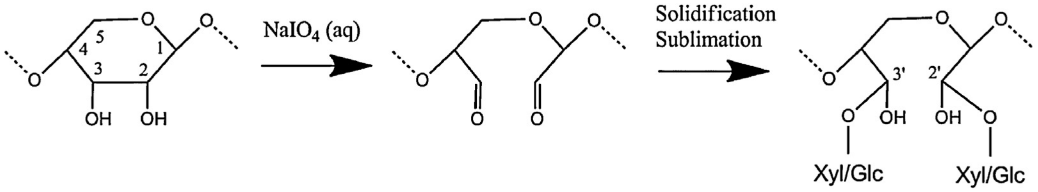

Fig. 2. Proposed reactions involved in cross-linking of xylan–cellulose nanocrystal composite hydrogels during freeze-casting.