Reactive & Functional Polymers 85 (2014) 157–166

Contents lists available at ScienceDirect

Reactive & Functional Polymers

journal homepage: www.elsevier.com/locate/react

Significance of xylan on the stability and water interactions of cellulosic nanofibrils

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ARTICLE INFO

Article history:
Received 5 July 2014
Received in revised form 26 August 2014
Accepted 28 August 2014
Available online 6 September 2014

Keywords:
Cellulose nanofibrils
Xylan
Electrosteric stability
Oxygen barrier
Films
Water interactions

ABSTRACT

In this paper, the significance of xylan on the behaviour of kraft birch pulp based nanofibrillated cellulose (CNF) is discussed. The influence of CNF xylan content on fibril morphology, charge and stability as well as on the film formation ability was investigated, and the features detected on nanoscale and on macroscale are compared. In addition to this, the ability of fibrils to uptake water molecules were investigated by bulk and surface sensitive methods which are dynamic water sorption analysis (DVS) and quartz crystal microbalance with dissipation monitoring (QCM-D) equipped with the humidity module, respectively. Surface xylan plays a significant role as an electrosteric stabilizer in dilute CNF dispersions when the surface forces are dominant whereas the removal of xylan drastically changes the CNF dispersion properties. The settling of the unstable CNF dispersions displays behaviour which is typical for hindered sedimentation. When considering thin nanoscale layers of CNF, nanofibrillated cellulosic materials with high content of surface xylan has somewhat higher ability to bind water molecules. However, it seems that in more concentrated CNF dispersions where the fibrillar network itself plays also a decisive role, especially with respect to film formation ability, the impact of xylan diminishes. Solvent cast macroscale CNF films are still enough dense to maintain good oxygen barrier performance at higher humid conditions although agglomeration tendency of fibrils is higher due to the excessive xylan removal. These findings are of high relevance when considering nanocellulosic materials, especially in the form of gels and films, as templates for high added value material solutions.

1. Introduction

Due to the unique physical features, e.g. high strength and stiffness of nanoscaled cellulosic materials (cellulose nanofibrils (CNF), microfibrillated cellulose (MFC) or cellulose nanocrystals (CNC)), there is a growing interest for seeking novel application areas [1–5]. The main reasons for the growing interest in CNF and MFC are the development of energy efficient and up-scalable production methods [6–8] and the extraordinary properties of this renewable material [9,10]. High aspect ratio and large interfacial area with an enhanced hydrogen bonding capability compared to native fibres enable the inherent gel formation [6] which makes it suitable to be incorporated in applications such as thickeners and emulsifiers for e.g. food, cosmetics and paints. Besides, the inherent film formation tendency of fibrils upon drying together with the facile and up-scalable film production methods [11–13], should open up numerous new opportunities for highly functional (nano)materials to be utilized e.g. as packaging materials [14], in electronics [15] and in diagnostics [16].

The main drivers to utilize nanoscaled lignocellulosic materials have been the sustainability trend, increasing prices of petroleum and possibility to gain additional functionalities which biobased building blocks may offer. In order to significantly improve and develop functional (nano)material structures using biomass derived building blocks, the understanding of the interfacial interactions becomes of high relevance. Nanocellulosic materials rarely exist as pure cellulose, on the contrary, plant derived cellulose nanofibrils contain hemicelluloses, lignin and wood extractives depending on the pulp source and processing. For example, birch kraft pulp based cellulosic nanofibrils utilized in this study contain approximately 23 wt% of glucuronoxylan, major hemicellulose present in hardwood [17]. Especially the accessible xylan located on fibril surface has a decisive role when dealing with interfacial interactions, physical properties and performance of new, advanced biomaterials [18–20]. On the other hand, the removal

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http://dx.doi.org/10.1016/j.reactfunctpolym.2014.08.011
1381-5148/

of xylan when processing of cellulosic biomass to green biorefineries have also been an active subject and several biomass pre-treatments have been developed, in order to recover hemicelluloses and use them in a more profitable pathway [21]. The potential of xylan has been seen for example in new bio-derived films and coatings, where it can be used in packaging applications as well as edible coatings and medical applications [22–26].

However, the impact of xylan removal on the properties of remaining cellulosic material is not trivial and the association of cellulose and xylan within biomass has been discussed in several studies. Cellulose fibrils are coated with hemicelluloses, which then form larger units that are embedded in a lignin–hemicellulose matrix [17]. In several studies, hemicelluloses have been noticed to have an impact in the aggregation behaviour of the cellulose by affecting the crystalline structure and changing the dimensions of the cellulose microfibrils [27–30]. Xylan has affinity towards fibres [31] and it also re-adsorbs onto fibres at the end of pulp cooking process with an impact on final properties of such fibres [32,33]. Few studies suggest that the presence of xylan on pulp fibres improves paper strength [34,35] since the presence of hemicelluloses promotes the formation of bond within cellulosic fibres. Thus, low hemicellulose content pulps are not desired for manufacture of high-quality paper and board, but they are a requisite for the production of dissolving-grades pulps [36]. With the increase in the current industrial interest on utilization of nanocelluloses for different applications, those pulps destined to the production of nanocellulose have a potential to be integrated in the biorefinery concept, as an alternative of hemicellulose source. To this end, deeper understanding on the effect of the removal of xylans on the final properties of these nanocelluloses is needed.

In this work the significance of glucuronoxylan on molecular level and macroscale level behaviour of cellulosic nanofibrils (CNF) is elucidated. The influence of xylan content on nanocellulosic fibril morphology, charge, colloidal stability as well as on film formation tendency and their oxygen barrier performance has been systematically investigated using a series of CNF grades with variable xylan content. In addition, the water interactions of CNF with respect to xylan content were revealed using bulk approach (dynamic vapour sorption, DVS, analysis) and surface sensitive approach (QCM-D equipped with humidity chamber).

2. Experimental

2.1. Materials

2.1.1. Pulp

Elemental chlorine free (ECF) never-dried bleached birch kraft pulp (UPM-Kymmene Oyj, Pietarsaari) was used as a raw material for the production of nanofibrillated cellulose grades (CNF) with variable xylan content. In order to control the fibre swelling and to enhance the fibrillation, the carboxyl groups of the pulp were converted to the sodium form prior to the fibrillation according to the method described previously [37]. Briefly, the method includes washing out the metal counterions from the pulp at low pH (0.01 M HCl, pH < 3). After filtration and washing with deionized water, conversion of the carboxyl groups into their sodium form is achieved by mixing the pulp with a discrete amount of 0.005 M $NaHCO_3$ solution. Finally, pH was set to slightly alkaline and rinsing with deionized water was performed in order to remove excess salt.

2.2. Methods

2.2.1. Preparation of pulps with variable xylan content

Birch kraft pulps of decreasing xylan content were prepared by selective and targeted xylan hydrolysis using purified *Trichoderma reesei* Xyl II (pI9) xylanase [38]. Hydrolysis was performed in deionized water at 45 °C for variable times (3, 24 and 68 h) and enzymatic action was terminated by soaking the pulps in a hot water bath (90 °C, 15 min). Carbohydrate composition of the pulps were analysed by HPLC after the enzymatic total hydrolysis to monosaccharides was achieved [39]. Charge of the pulps was measured using the standard titration method SCAN CM 65:02.

2.2.2. Preparation of nanofibrillated cellulose

Pre-refining of the pulp was carried out with a Voith laboratory scale refiner (LR-1, Voith) to ease feeding and to avoid clogging during fibrillation. Fibrillation was performed using a high-pressure fluidizer (Microfluidizer EH110, Microfluidicies Corp.) after diluting pulps to a consistency of 1.8% with deionized water and pre-dispersing using Dispermat (VMA Getsman Gmbh) at 3400 rpm for 60 min. Several successive passes through two differently sized chamber pairs were performed in order to induce efficient fibrillation. First, the pulps passed a chamber pair with diameters of 400 μm and 200 μm at a pressure of 1350 bars, followed by 17 passes through a chamber pair with diameters of 400 μm and 100 μm at a pressure of 1850 bars. Final material appearance was that of a viscous, gel-like material. Samples were then stored at +4 °C until further used.

2.2.3. Microscopic analysis of CNF with variable xylan content by AFM and SEM

The size of nanofibrillated cellulose grades with different xylan content was analysed using Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM). AFM imaging was performed using a Nanoscope IIa Multimode scanning probe microscope (Digital Instruments Inc., Santa Barbara, CA USA). The nanofibril samples were prepared by spincoating a dilute CNF dispersion on silica surface as described in Ahola et al. [40]. The images were scanned in tapping mode, in air using silicon cantilevers (IMasch, Tallinn, Estonia) with nominal resonance frequencies of 320–360 kHz. No image processing except flattening was made and at least 5 areas on each sample were measured.

SEM imaging was performed using LEO DSM 982 Gemini FEG-SEM (Noran Instruments Inc. Middleton, USA). The nanofibril samples were first solvent exchanged to acetone and the removal of acetone was carried out by critical point drying method (CPD, Bal-Tec CPD 030 Critical Point Dryer) using CO_2 as the transition liquid. Prior to the SEM analysis the CNF samples were sputter coated (Agar Automatic Sputter Coater, Stansted, UK) with platinum to improve specimen conductivity and examination was performed using an acceleration voltage of 2.0 keV.

2.2.4. Crystallinity analysis of pulp and CNF with variable xylan content by WAXS

Freeze-dried pulp and CNF samples were pressed into metal rings of thickness of 1 mm and wide-angle X-ray scattering (WAXS) was measured under perpendicular transmission geometry. The used setup consisted of a Seifert ID 3003 X-ray generator equipped with an X-ray tube producing Cu Kα radiation (wavelength 1.54 Å). The X-ray beam was monochromatized with a Montel multilayer and the scattering pattern was recorded by a two-dimensional image plate detector (MAR345, Marresearch). The measured intensity was corrected for measurement geometry, angle-dependent absorption and backgrounds due to air-scattering and noise from to the image reading of the detector. Crystallinity and crystal width in the [200] direction of cellulose Iβ were obtained from the corrected WAXS intensities by applying the fitting procedures described in Penttilä et al. [41].