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Preparation of reactive fibre interfaces using multifunctional cellulose derivatives

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ABSTRACT

Cellulose fibres have poor reactivity and limited potential for surface engineering with advanced chemical functionalization in water. In this work, cellulose fibres were decorated with azide functions by charge-directed self-assembly of a novel water-soluble multifunctional cellulose derivative yielding reactive fibres. Propargylamine and 1-ethynylpyrene were utilized as a proof of concept that alkyne molecules may react with the azide functions of the reactive fibres via copper(I)-catalyzed azide-alkyne Huisgen cycloaddition (CuAAc) reaction in mild conditions. Chemical characterization of the fibres was carried out using classical techniques such as Raman-, fluorescence-, and UV–vis spectroscopy. Among other techniques, time-of-flight secondary ion mass spectrometry (ToF-SIMS), X-ray spectroscopy (XPS), two-photon microscopy (TPM), and inductively coupled plasma mass spectrometry (ICP-MS) were useful tools for additional characterization of the fibres decorated with amino- or photoactive groups. The information gathered in this work might contribute to the basis for the preparation of reactive cellulose-based interfaces with potential application in CuAAc reactions.

1. Introduction

Wood is one of the most important products in nature. Beyond its usage as a building material, for tools or as energy resource, wood is the primary source for the production of pulp (Fengel & Wegener, 1984). Approximately 160 million tonnes of pulp are being produced worldwide every year and most commonly used for the manufacture of paper and paperboard (FAO, 2012). In the context of the emerging biorefinery concept and due to the limited economic growth in the field of classical pulp- and paper production, an intense search for added-value materials from wood pulp has been reported recently. For example, functional fibres (Grigoray, Wondraczek, Heikkilä, Fardim, & Heinze, 2014; Martínez, Phillips, & Whitesides, 2010; Vega et al., 2013; Zhou, Yang, & Zhou, 2014), cellulose-based nanomaterials (Dufresne, 2012; Filpponen et al., 2012; Junka et al., 2014; Kettunen née Pääkkö, 2013; Klemm et al., 2011; Missoum, Belgacem, & Bras, 2013; Moon, Martini, Nairn, Simonsen, & Youngblood, 2011; Peresin, Habibi, Zoppe, Pawlak, & Rojas, 2010), cellulose beads (Gericke, Trygg, & Fardim, 2013), cellulose-based composites (Khalil, Bhat, Ireana, & Yusra, 2012; Huber et al., 2012; Lange, Touaiti, & Fardim, 2013; Narewska, Lassila, & Fardim, 2014; Satyanarayana, Arizaga, & Wypych, 2009) have been successfully prepared at the laboratory scale.

Functional fibres, which possess particular functionalities while preserving the excellent mechanical properties of the traditional pulp fibres, can be obtained by different chemical, enzymatic, or physical treatments (Elegir, Kindl, Sadocco, & Orlandi, 2008; Kim, Zille, Murkovic, Güebitz, & Cavaco-Paulo, 2007; Li, Tabil, & Panigrahi, 2007; Persson, 2004; Qiu & Hu, 2013). Although functional fibres show an enormous potential, currently there are only a few examples of their pilot- or larger scale production (Cellgaia, 2014; Green fiber, 2014; Sentinel, 2014). It seems that pulp industry is reluctant to adapt their production lines to functional fibres because of different challenges they might have to face. For example, chemical modifications of wood fibres may be associated both with harsh conditions or complicated procedures (Fox, Li, Xu, & Edgar, 2011; Gruber, Granzow, & Ott, 1998; Vuoti et al., 2013). In addition to that, severe condition reactions may cause cellulose

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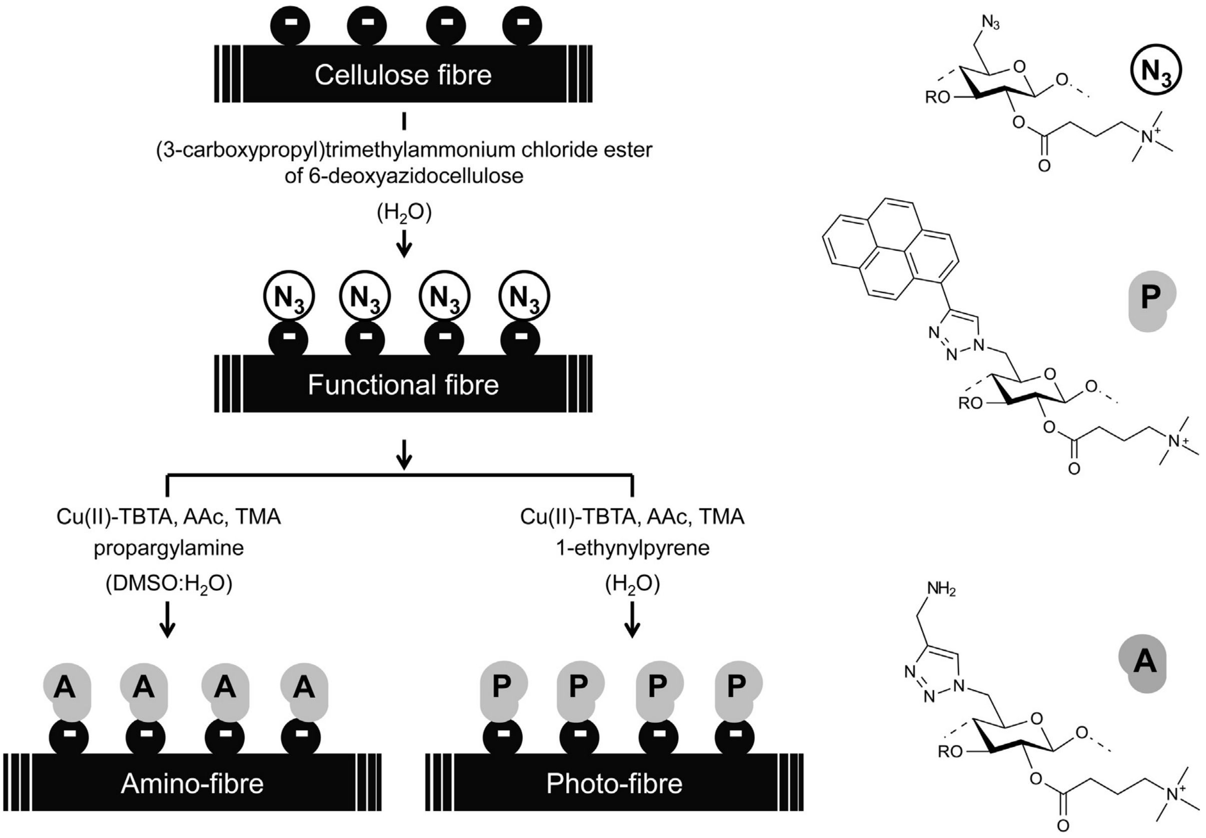

Scheme 1. Synthesis scheme for the preparation of cellulose fibres decorated with photoactive molecules (photo-fibres) and amino functional groups (amino-fibres) prepared from cellulose fibres decorated with azide functions (reactive fibres). Cu(II)-TBTA, Cu(II)-tris[(1-benzyl-1H-1,2,3-triazol-4-yl)methyl]amine complex solution; AAc, ascorbic acid; TMA, triethylammonium acetate buffer.

degradation with the inherent loss of the mechanical properties that might result in low-yield processes (Heinze & Liebert, 2001). Enzymatic treatments may be an attractive alternative to chemical treatments since they can be carried out under mild conditions, but methods still need to be optimized. On top of this, in most cases the novel materials are meant as much specialized products with great added-value but low demand. Therefore, it is hardly surprising that changes in the production line are not worth considering from the industrial point of view.

The approach discussed here is trying to connect the dots between the increasing demands of natural materials, the thriving pulp- and papermaking industries and the well-developed chemistry of polysaccharide derivatives. We are focusing the efforts on simple and sustainable processes that enable the production of functional fibres. Our approach relies on the following arguments: (i) It is possible to prepare highly engineered multifunctional polysaccharide derivatives decorated with functional groups related to the desired application on basis of current the knowledge, (ii) ionic groups of polysaccharide derivatives trigger their water solubility, and, therefore, it is easy to apply these compounds on the production line of pulp mills (Zhang, 2001), (iii) the ionic, particularly the cationic groups, allow the charge directed self-assembly of the multifunctional cellulose derivatives on wood fibres yielding functional fibres (Gustafsson, Larsson, & Wåberg, 2012; Lingström & Wågberg, 2008; Vega et al., 2013).

The use of direct self-assembly of multifunctional cellulose derivatives on wood pulp fibres has many advantages. For example, the challenging step of chemical modification of cellulose is separated from the production of the traditional wood fibres. In addition, the sorption mechanism of cationic derivatives can be well described (Ankerfors, Lingström, & Wåberg, 2009; Gustafsson, Larsson, & Wågberg 2012; Lingström, & Wåberg, 2008; Vega et al., 2013; Wåberg, 2000) and, therefore, the amount of specialized cellulose derivative needed to implement a particular function to the bulk fibre is easy to control. Moreover, the sorption experiments are carried out in aqueous medium and room temperature, thus preventing the degradation of the wood pulp fibres during the treatment.

In the present paper, the preparation of cellulose fibres decorated with azide groups – named as reactive fibres – is described. The functionalization of bleached Kraft pine fibres was successfully achieved using (3-carboxypropyl)trimethylammonium chloride ester of 6-deoxyazidocellulose (N_3-cell$^+$) as a modifying agent in aqueous solution. The sorption process was studied using UV–vis spectroscopy. Propargylamine and 1-ethynylpyrene resulted covalently linked to azide functions of the functionalized fibre interfaces via copper(I)-catalyzed alkyne-azide Huisgen cycloaddition reaction (CuAAc) yielding amino-fibres and photo-fibres, respectively (Scheme 1). The outermost layer of amino-fibres was studied using X-ray spectroscopy (sampling depth of ~1 nm). The concentration of amino groups on these fibres was determined using a colorimetric method. The photo-fibres were characterized using Raman-, fluorescence-, and UV–vis spectroscopy. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) and field-emission scanning electron microscopy (FE-SEM) were used for studying the chemical composition of the extreme layer (sampling depth of ~1 nm) and the morphology of photo-fibres, respectively. In addition, the distribution of the fluorophores on the photo-fibres was studied using two-photon microscopy (TPM). The amount of copper that remains on the fibres after CuAAc reaction was determined using