

A method for the heterogeneous modification of nanofibrillar cellulose in aqueous media

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ABSTRACT

Cellulosic substrates were modified by using sequential adsorption of functionalized carboxymethyl cellulose (CMC) and “click” chemistry in aqueous media. First, the effect of degree of substitution (DS), and level of functionalization as well as ionic strength of the medium were systematically investigated in situ by using quartz crystal microbalance with dissipation (QCM-D) in terms of the extent of adsorption of propargyl and azido functionalized CMC. It was found that the functionalization of CMC did not prevent its adsorption on cellulose. However, it was only effective in the presence of electrolytes. Moreover, the adsorption was found to be more efficient for the functionalized CMCs with low initial DS. Next, “click” chemistry, copper (I)-catalyzed azide-alkyne cycloaddition reaction (CuAAC), was carried out for covalent attachment of different molecules on the pre-functionalized ultrathin cellulose films. The modified cellulosic surfaces were further characterized using AFM imaging and XPS. Finally, the method was successfully used in modification of nanofibrillar cellulose (NFC) in aqueous media.

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1. Introduction

The copper (I)-catalyzed 1,3-dipolar cycloaddition of alkynes and azides (CuAAC) has sparked an increased attention because it is one of the few reactions that occurs between chemically stable functional groups (Scheme 1, step 2) (Iha et al., 2011; Kolb, Finn, & Sharpless, 2001; Rostovtsev, Green, Fokin, & Sharpless, 2002; Tornøe, Christensen, & Meldal, 2002). Moreover, it is known that the CuAAC reaction tolerates both water and oxygen which allows the use of mild reaction conditions with a large variety of functionalized molecules. This is encouraging especially in terms of biomaterials which are usually highly sensitive toward harsh reaction conditions. In fact, cellulose modifications using CuAAC “click” reaction have already been demonstrated (Filpponen & Argyropoulos, 2010; Liebert, Hänsch, & Heinze, 2006; Pahimanolis et al., 2011).

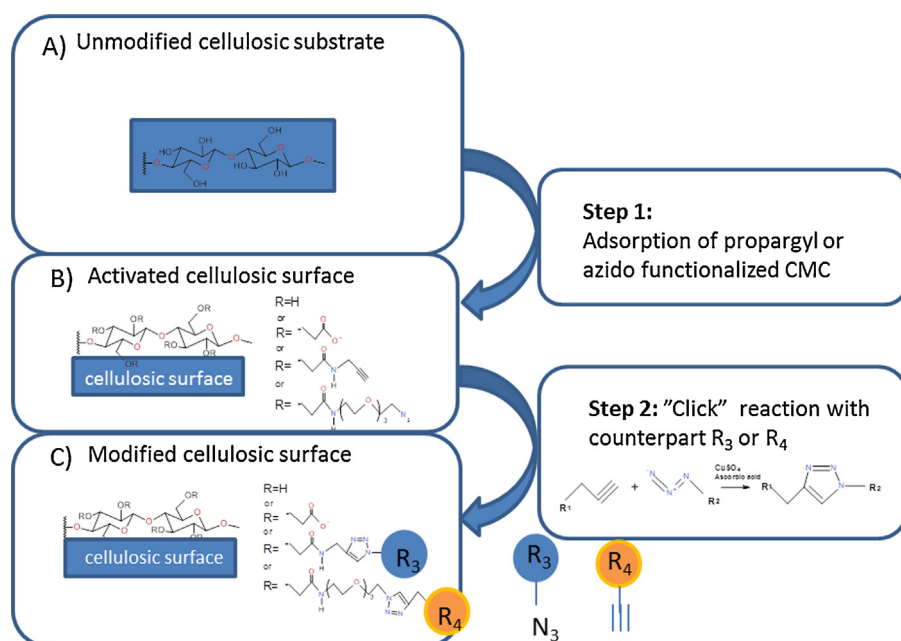
Cellulose is a biopolymer with a tendency for strong hydrogen bonding which gives it extremely good strength properties (Eichorn et al., 2010). Direct chemical modification, such as etherification and esterification of cellulose is often challenging because of its high stability and hydrophilicity (Carter Fox, Li, Xu, & Edgar, 2011). In addition, to preserve the native cellulose

structure, the chemical reactions cannot be made in the dissolved homogeneous state. Moreover, harsh chemical modifications of cellulose usually result in lower degree of polymerization and weaker inter- and intramolecular hydrogen bonding of the cellulose chains. In dry cellulosic materials, such as films or paper, this often means substantially lower mechanical properties of the material (Henriksson, Berglund, Isaksson, Lindström & Nishino, 2008). Therefore, alternative methods to modify cellulosic objects exclusively on the surface by using functionalized polysaccharides have been developed (Filpponen et al., 2012; Xu, Spadiut, Araújo, Nakhai, & Brumer, 2012; Zhou, Rutland, Teeri, & Brumer, 2007). These methods combine chemical or enzymatic modification of water-soluble polysaccharides and their tendency to adsorb irreversibly on cellulose. It is well known that certain water-soluble and linear polysaccharides have an ability to increase the adhesion and decrease the friction between cellulosic fibers as well as increase the tensile strength of paper in traditional papermaking applications (Leech, 1954; Lindström, Wågberg, & Larsson, 2005; Schönberg, Oksanen, Suurnäkki, Kettunen, & Buchert, 2001). In general, the use of polysaccharides for introducing diverse functional groups on the surface of cellulosic materials has a potential to replace some of the traditional synthetic methods and may even provide new modification routes.

The polymer chains of cellulose are assembled in the form of fibrils which are approximately 3–20 nm (Klemm, Heublein, Fink, & Bohn, 2005) in width and are called elementary fibrils. In plant

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Scheme 1. Schematic illustration of the generic method to modify cellulosic surfaces by adsorption of an azido or propargyl functionalized CMC (step 1) followed by CuAAC reaction with various probes containing either an alkyne or azide group (step 2).

cell wall these aggregate even into larger macroscopic cellulosic fibers. The preparation of micro- or nanofibrillar cellulose (NFC) from plants and wood consist on the deconstruction of their hierarchical structure. The intrinsic features of NFC include excellent strength properties, low weight, high aspect ratio, biodegradability and renewability (Klemm et al., 2011).

In the present work we use a generic method to modify cellulosic surfaces (Filpponen et al., 2012) via sequential adsorption of functionalized (azido or propargyl) carboxymethyl cellulose (CMC) and a “click” reaction (Scheme 1). The proof-of-principle of this method has already been established (Filpponen et al., 2012) but here, the objective was to probe further the parameters which determine the adsorption and the “click” reaction. Two different degrees of substitution (DS) and levels of functionalization of CMCs were systematically investigated. The adsorption of pre-functionalized CMCs was used to “activate” ultrathin cellulose model films and the effect of ionic strength on the adsorption was followed by using quartz crystal microbalance with dissipation (QCM-D). Activated cellulose surfaces were further modified in situ by using CuAAC reaction with various clickable molecules. The modified cellulose model surfaces were characterized by using atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). Finally, we demonstrate that the current methodology can be applied to the modifications of NFC gel – an important piece of information considering the huge potential of NFC in modern materials science.

2. Materials and methods

2.1. Chemicals and solutions

All chemicals used were of analytical grade. Ultrapure MilliQ-water (Millipore Synergy UV unit; Millipore S.A.S. Molsheim, France) was used for dilutions. Two different sodium carboxymethyl celluloses (Na-CMCs, 250 kDa), CMC1 and CMC2 of nominal DS of 0.7 and 1.2, respectively were supplied by Sigma–Aldrich and purified prior to use by dialysis followed by freeze-drying. All the CMC solutions were prepared by dissolving the powder in ultrapure MilliQ-water by stirring the solution

overnight. The samples were further diluted to a given concentration, and the ionic strengths were adjusted with NaCl. The DS of the purified CMC samples were calculated based on their charge density measured with polyelectrolyte titration (Hiroshi, 1952). 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) and N-hydroxysuccinimide (NHS) were purchased from Fluka and Thermo Scientific, respectively. Methoxy polyethylene glycol azide (OME-PEG azide, 20 kDa), Bovine Serum Albumin (BSA, 66 kDa) and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (98+%) were purchased from Sigma–Aldrich. L-Ascorbic acid (99%) was purchased from Acros Organics. Trimethylsilyl cellulose (TMSC) was synthesized from cellulose powder (spruce, Fluka), according to a previously published method (Kontturi, Thüne, & Niemantsverdriet, 2003). The fully bleached (bleaching sequence Acid wash-Ozone/Chlorine Dioxide-Alkaline Extraction with oxygen and peroxide-Chlorine Dioxide-Peroxide, A-Z/D-EOP-D-P) birch pulp was used as a raw material for the preparation of nanofibrillar cellulose (NFC). These pulps were supplied by UPM Kymmene kraft mill (Pietarsaari, Finland). The Kappa number (KN) of precursor birch pulp was <1, degree of polymerization (DP) of 2100 and hemicellulose content up to 25% (Solala et al., 2011; Ferrer et al., 2012). Prior to fluidization, it was fractionated (200 mesh, SCAN-M 6:69) and washed to sodium form (Swerin, Ödberg, & Lindström, 1990). The molecular structures of cellulose, CMC, propargyl functionalized CMC and azido functionalized CMC, as well as the counterpart molecules, i.e., dansyl-alkyne, OME-PEG azide and BSA-alkyne are shown in Fig. 1.

2.2. CMC functionalization

The carbodiimide activation of CMC was done according to Filpponen et al. (2012). Two different CMCs (CMC1 and CMC2) were activated to two different levels. 100 mg of CMC was dissolved in distilled water and mixed overnight. The CMC solution was diluted to 2 g dm^{-3} with NaAc/HAC buffer (pH 4.5, $I = 10 \text{ mM}$) and the ionic strength was adjusted to 50 mM with NaCl. Next, 1 mmol (CMC1) or 1.5 mmol (CMC2) of EDC, 4 mmol (CMC1) or 6 mmol (CMC2) of NHS and either 1.5 mmol (higher amount, CMC2), 1 mmol (higher amount, CMC1) or 0.8 mmol (lower amount, CMC2 and CMC1) of the amine-group containing molecule (propargylamine for

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