Carbohydrate Polymers 164 (2017) 49–56

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

Nonspecific protein adsorption on cationically modified Lyocell fibers monitored by zeta potential measurements☆

Claudia Payerl[a,b], Matej Bračič[c], Armin Zankel[d], Wolfgang J. Fischer[b,e], Manuel Kaschowitz[a], Eleonore Fröhlich[f], Rupert Kargl[a,c], Franz Stelzer[a], Stefan Spirk[a,b,c,e,*]

[a] Institute for Chemistry and Technology of Materials, Graz University of Technology, Stremayrgasse 9, 8010 Graz, Austria
[b] CD-Laboratory for Fiber Swelling and Paper Performance, Inffeldgasse 23(A), 8010 Graz, Austria
[c] Laboratory for Characterization and Processing of Polymers (LCPP), University of Maribor, Smetanova 17, 2000 Maribor, Slovenia
[d] Graz Centre of Electron Microscopy, and Institute of Electron Microscopy, Graz University of Technology, Steyrergasse 17, 8010 Graz, Austria
[e] Institute for Paper, Pulp and Fiber Technology, Inffeldgasse 23, 8010 Graz, Austria
[f] Center for Medical Research, Medical University of Graz, Stiftingtalstraße 24, Graz, Austria

ARTICLE INFO

Article history:
Received 29 September 2016
Received in revised form 23 January 2017
Accepted 24 January 2017
Available online 25 January 2017

Keywords:
Lyocell fibers
Protein adsorption
Zeta potential
Tenacity
Chitosan

ABSTRACT

Nonspecific protein deposition on Lyocell fibers via a cationization step was explored by adsorption of two different *N,N,N*-trimethyl chitosan chlorides (TMCs). Both, the cationization and the subsequent protein deposition steps were performed and monitored *in situ* by evaluating the zeta potential using the streaming potential method. Both employed TMCs (degree of substitution with N^+Me_3Cl groups: 0.27 and 0.64) irreversibly adsorb on the fibers as proven by charge reversal (−12 to +7 mV for both derivatives) after the final rinsing step. Onto these cationized fibers, BSA was deposited at different pH values (4, 5, and 7). Charge titrations revealed that close to the isoelectric point of BSA (4.7), BSA deposition was particularly favored, while at lower pH values (pH 4), hardly any adsorption took place due to electrostatic repulsion of the cationic fibers and the positively charged BSA. This work sets the foundation for further investigations to use zeta potential measurements for protein adsorption studies on fibrous materials.
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1. Introduction

The immobilization of functional layers on cellulosic surfaces has seen a tremendous increase of research activities over the past two decades. One emerging area has been the equipment of cellulosic materials with biomolecules (Hasani, Cranston, Westman, & Gray, 2008; Mohan et al., 2014; Mohan, Ristic et al., 2013). In terms of applications, the main motivation is to generate biocompatible, potentially implantable cellulose-based biosensors (Kargl et al., 2013; Orelma, Filpponen, Johansson, Laine, & Rojas, 2011; Orelma, Johansson, Filpponen, Rojas, & Laine, 2012). In this context, cellulose offers an advantage such as a rather low nonspecific binding of proteins which allows for selective anchoring of bioactive molecules in a physiological environment (Filpponen et al., 2012). Previous studies on different types of cellulosic materials revealed that bovine serum albumin (BSA), a widely used marker to assess nonspecific binding, hardly adsorbs on cellulosic materials (Orelma et al., 2011). This behavior originates from several factors, namely the amphiphilic nature of cellulose, combined with its rather high degree of swelling, hampering nonspecific binding since both, the highly hydrated cellulosic material and the protein, need to be dehydrated upon interaction (Norde & Lyklema, 1991). Further, BSA and other nonspecific markers mainly adsorb nonspecifically via hydrophobic interactions (Roach, Farrar, & Perry, 2005; Roach, Farrar, & Perry, 2006).

For many applications, the interaction capacity of proteins must be controlled in order to achieve a controllable device. In this context, several different approaches do exist which use either chemical grafting of functional groups or simple physical adsorption of biocompatible species such as other polysaccharides for instance (Kargl et al., 2012; Liu, Choi, Gatenholm, & Esker, 2011; Miletzky et al., 2015; Mishima, Hisamatsu, York, Teranishi, & Yamada, 1998; Mohan, Zarth et al., 2013; Taajamaa, Rojas, Laine, Yliniemi, & Kontturi, 2013). Depending on the isoelectric point (IP) of the chosen protein and the adsorption conditions (pH, temperature, ionic strength), either negatively or positively charged

☆ Members of the European Polysaccharide Network of Excellence (EPNOE).

* Corresponding author at: Institute for Chemistry and Technology of Materials, Graz University of Technology, Stremayrgasse 9, 8010 Graz, Austria.
E-mail address: stefan.spirk@tugraz.at (S. Spirk).

http://dx.doi.org/10.1016/j.carbpol.2017.01.088
0144-8617/© 2017 Published by Elsevier Ltd.

polysaccharides can be employed to tune the amount of deposited proteins. In this context, carboxymethyl celluloses, cationic celluloses and chitosans have been reported in literature, whereas in most cases thin films have been studied (Hasani et al., 2008; Orelma et al., 2011; Salas, Rojas, Lucia, Hubbe, & Genzer, 2013; Strasser et al., 2016). The advantage of thin films is their rather uniform appearance in terms of morphology, porosity and chemical composition. Further, surface sensitive methods do exist to monitor the adsorption behavior of such biomolecules in real time such as quartz crystal microbalance with dissipation (QCM-D) and surface plasmon resonance (SPR). The 2D confinement of such films can give rise to basic interaction capacities of cellulose with such biomolecules but the rather complex morphology and porosity of real fiber samples make direct comparisons difficult or even impossible to establish. On the other hand, there are only limited tools available to study the adsorption of biomolecules on fibers *in situ* and most papers deal with the *ad mortem* analysis of the samples after adsorption has been completed revealing the kinetics unexplored. One of the few methods capable to monitor changes in real time on fibers is to follow the change in the zeta potential of the fibers during the adsorption using the streaming potential method (Jacobasch, 1989). This method exploits changes in the charge of the samples upon adsorption and allows for the analysis of interaction capacities and to investigate adsorption processes of a wide range of materials with cellulose fibers ranging from inorganic clays to synthetic polymers and biopolymers such as chitosan, carboxymethyl cellulose and proteins for instance. Most biomolecules are charged and therefore such experiments can be employed to gain insights into their interaction capacity with cellulosic fibers by evaluation of the change in zeta potential during the adsorption (Hubbe, Rojas, Lucia, & Jung, 2007; Ribitsch, Stana-Kleinschek, Kreze, & Strnad, 2001; Ristić, Hribernik, & Fras-Zemljič, 2015; Stana-Kleinschek & Ribitsch, 1998; Zemljič, Peršin, Stenius, & Kleinschek, 2008).

In this study, we aim at a detailed investigation of biomolecule adsorption on cellulosic fibers by monitoring the change in zeta potential. As model system, we employ regenerated cellulose staple fibers (Lyocell) which are coated with *N,N,N*-trimethyl chitosan chlorides (TMC) having different degrees of substitution. Afterwards, BSA adsorption at different pH values is performed. All these coating experiments are performed *in situ* using the streaming potential method and characterization is further complemented by low voltage scanning electron microscopy (LV-SEM) and charge titration studies after the adsorption experiments have been completed. Mechanical properties were investigated in order to track changes induced by the adsorbed polysaccharide and the subsequent protein layer.

2. Materials and methods

2.1. Materials

N,N,N-trimethyl chitosan chloride (TMC, M_w: 50–80 kDa, medical grade) with two different degrees of substitution (TMC_L: Degree of acetylation: 0.2, Degree of substitution (DS): with $NMe_3^+Cl^-$: 0.27; TMC_H: Degree of acetylation: 0.32, Degree of substitution (DS) with $NMe_3^+Cl^-$: 0.64) was purchased from Kitozyme S.A. (Herstal, Belgium). Aqueous TMC solutions (0.1 g/mL) were prepared and the pH value was adjusted to seven using HCl and NaOH (0.1 M).

Lyocell staple fibers (trade name TENCEL Standard) were kindly provided by Lenzing AG, Austria. The titer and the length of the fibers were 1.3 dtex and 3.8 mm, respectively.

BSA was purchased from Sigma-Aldrich, Austria, and used as received. BSA solutions (c = 0.1 g/mL) at pH 4.0, 5.0 and 7.0, were prepared in 10 mM KCl aqueous solution with MilliQ water (resistivity 18 MΩ cm). The pH value was adjusted by adding 0.1 M NaOH or 0.1 M HCl solution.

2.2. Surface modification of cellulose fibers with TMC

In the first step, cellulose fibers were rinsed with 500 ml electrolyte solution (conductivity ~ 16 mV) to remove fiber finishing agents. After the rinsing step, a 10 mM KCl electrolyte solution was adjusted to pH 7, injected into the system and a baseline of pure cellulose was recorded in the zeta potential measurements. TMC (0.1 g/ ml) was subsequently dissolved in the electrolyte solution and the *in-situ* adsorption thereof was again recorded using the zeta potential. All experiments have been performed in three repetitions.

2.3. BSA adsorption on TMC- modified cellulose fibers

BSA adsorption onto the modified and non-treated fibers was studied at pH values of 4, 5 and 7 in 10 mM KCl electrolyte solution (c_{BSA} = 0.1 mg/ml). The adsorption process was monitored until an adsorption plateau was observed and then the system was rinsed with the respective electrolyte solution to remove loosely bound BSA molecules. All experiments have been performed in three repetitions.

2.4. Zeta potential measurements/electrokinetic measurements

The Streaming Potential was recorded using the SurPASS, an Electro kinetic Analyzer (Anton Paar GmbH, Graz, Austria,) and the resulting zeta potential was calculated according to the Smoluchowski, Eq. (1). The SurPASS is equipped with Ag/AgCl- electrodes which are continuously determining the streaming potential. The sample was applied as a fiber plug between two perforated electrodes using the equipped cylindrical cell of the instrument which allows for measuring fluid streaming through the fiber plug and the detection of the potential.

The zeta potential ζ was calculated according to Smoluchowski (1)

$$\zeta = \frac{dU}{dp} \times \frac{\eta}{\varepsilon_r \times \varepsilon_o} \times \kappa \quad (1)$$

where U is the streaming potential, p is the pressure, ε_r is the relative permittivity of the fluid and ε_0 the dielectric constant and the vacuum permittivity, η is the viscosity and κ the conductivity of the fluid (Delgado et al., 2005). The pH-dependence of zeta potential was determined in the presence of 10 mM KCl solution. If the properties of the liquid phase remain constant, the electrokinetic potential of fibers is influenced by several parameters: chemical constitution, polarity of the surface region, microstructure of the fiber, such as porosity and crystallinity, and swelling properties in water.

2.5. Tensile testing

The tenacity (cN/dtex) and elongation at break (%) of single Lyocell fibers including blank samples were determined according to ISO 5079 using a Vibroskop 400 (Lenzing Technik Instruments) under defined conditions (50% humidity, 25 °C). Gauge length, preloading and cross-head speed were 20 mm, 70 mg, 20 mm/min, respectively. 20 fibers for each sample were tested.

2.6. Low voltage scanning electron microscopy (LVSEM)

While conventional scanning electron microscopy (CSEM) uses an electron beam with a landing energy of the electrons between

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