



Research Paper

Layer-by-layer assembled hydrophobic coatings for cellulose nanofibril films and textiles, made of polylysine and natural wax particles



Nina Forsman^{a,1}, Alina Lozhechnikova^{a,1}, Alexey Khakalo^a, Leena-Sisko Johansson^a, Jari Vartiainen^b, Monika Österberg^{a,*}

^a Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto University, P.O. Box 16300, FI-00076 Aalto, Finland

^b VTT Technical Research Centre of Finland Ltd, Biologinkuja 7, P.O. Box 1000, FI-02044 Espoo, Finland

ARTICLE INFO

Article history:

Received 22 February 2017

Received in revised form 2 June 2017

Accepted 3 June 2017

Available online 6 June 2017

Keywords:

Layer-by-layer assembly

Poly-L-lysine

Carnauba wax

Textile

Cellulose nanofibril films

Hydrophobicity

ABSTRACT

Herein we present a simple method to render cellulosic materials highly hydrophobic while retaining their breathability and moisture buffering properties, thus allowing for their use as functional textiles. The surfaces are coated via layer-by-layer deposition of two natural components, cationic poly-L-lysine and anionic carnauba wax particles. The combination of multiscale roughness, open film structure, and low surface energy of wax colloids, resulted in long-lasting superhydrophobicity on cotton surface already after two bilayers. Atomic force microscopy, interference microscopy, scanning electron microscopy and X-ray photoelectron spectroscopy were used to decouple structural effects from changes in surface energy. Furthermore, the effect of thermal annealing on the coating was evaluated. The potential of this simple and green approach to enhance the use of natural cellulosic materials is discussed.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

In line with the principles of Green Chemistry (Jenck, Agterberg, & Droescher, 2004) we should strive to use renewable feedstock and raw materials, design safe chemicals and products and use safe solvents and reactions conditions. Despite these declarations, only 9% of the organic material feedstock in the EU chemical industry was from renewable sources in 2011 (The European Chemical Industry Council, 2014). Out of the renewable materials, cellulose is maybe the most attractive due to its abundance and interesting properties. The use of cellulosic feedstock could be increased in several global industries, for example, in textile and packaging manufacturing. In 2013, 64% of the fibres produced globally were synthetic, while plastic packaging waste in Europe accounted for 15 million tons (CIRFS, 2016; Eurostat, 2016). Therefore, considering the scale of these industries, a small change towards sustainability would have a large impact. However, the hydrophilicity of cellulose makes it sensitive to moisture, thus often limiting its use. Consequently,

extensive research has been devoted to increasing the hydrophobicity of cellulosic materials and enhancing their barrier properties in wet or humid conditions.

In the textile field, wearable textiles are often desired to be waterproof but yet breathable at the same time. Most methods to produce such textiles rely on synthetic fibres (Horrocks & Anand, 2015). Commonly used production techniques include tuning the porosity of the material, so that the pores are large enough for water vapor to pass through, but small enough to stop liquid water permeation, or coating the fibres of the textile and leaving the pores uncoated (Mukhopadhyay & Vinay Kumar, 2008).

Biomimetic approaches to textile modification have also been suggested, mainly to achieve superhydrophobic or self-cleaning surfaces due to a combination of nano- and microscale roughness and low surface energy. The roughness has commonly been achieved by applying nanoparticles, like silica (Gao, Zhu, Guo, & Yang, 2009; Xue, Jia, Zhang, & Tian, 2009; Yu, Gu, Meng, & Qing, 2007), ZnO nanorods (Xu & Cai, 2008; Xu, Cai, Wang, & Ge, 2010) and carbon nanotubes (Liu et al., 2007). The low surface energy has been obtained by using different silane compounds (Gao et al., 2009; Xu & Cai, 2008; Xu et al., 2010), some of which also have fluorine in the structure (Xue et al., 2009; Yu et al., 2007). Gao et al. reported negligible changes in air permeability after the coating (Gao et al.,

* Corresponding author.

E-mail address: monika.osterberg@aalto.fi (M. Österberg).

¹ These authors contributed equally to this work.

2009), otherwise breathability/moisture buffering properties have not been reported for superhydrophobic substrates.

Another efficient method to introduce hydrophobicity to a fabric is polymer grafting directly onto the surface. Polyethylene glycol (Badanova, Taussarova, & Kutzhanova, 2014), 1,1,2,2-tetrahydroperfluorodecylacrylate (Tsafack & Levalois-Grützmaier, 2007) and 1H,1H,2H,2H-nonafluorohexyl-1-acrylate (Deng et al., 2010), among some others, have been grafted onto cotton to induce hydrophobicity. Badanova et al. reported that the air permeability was unchanged after the grafting reaction (Badanova et al., 2014), but otherwise no results for gas permeability or transfer were reported. Qi et al. successfully coated a poly(ethylene terephthalate) substrate with fluorocarbon using ion beam sputtering (Qi et al., 2002). A uniting factor for many of the existing coatings is the use of different fluorine compounds, which provide high hydrophobicity, but come at high cost and are potentially harmful for human health and the environment (Schultz, Barofsky, & Field, 2003). Other conventional chemical methods to increase hydrophobicity in plant fibres (and further on textiles) include acetylation and benzylation (Kalia, Thakur, Celli, Kiechel, & Schauer, 2013). The problem with chemical treatments, however, is that they often require large amounts of hazardous solvents and produce equally hazardous waste (Kalia et al., 2013).

Furthermore, the use of cellulosic feedstock in packaging could be increased through the application of cellulose nanofibril (CNF) films. Recent research advances have shown that CNF films could, due to their dense structure and good barrier properties, have a potential in packaging applications (Lavoine, Desloges, Dufresne, & Bras, 2012). The pure CNF films show good oxygen barrier properties at relative humidity (RH) below 65% (Österberg et al., 2013). To improve their barrier performance at higher RH, several techniques were proposed. Österberg et al. (2013) used a thick paraffin wax coating to hydrophobize the CNF film, while Liu et al. mixed CNF with clay and thus reduced the oxygen transfer rate at 95% RH (Liu et al., 2007). Other methods that proved effective for lowering the oxygen transfer rate include carboxymethylation pre-treatment, acetylation post-treatment or coating of the CNF films onto polymer films (Lavoine et al., 2012). Carboxymethylation and acetylation, as well as natural and synthetic wax coatings, were also found to lower the water vapor transfer rate of the CNF films (Lavoine et al., 2012; Spence, Venditti, Rojas, Pawlak, & Hubbe, 2011).

The layer-by-layer (LbL) deposition is a simple, low-cost, controllable and versatile method for surface modification, and is therefore an attractive alternative to chemical grafting on various cellulosic substrates, including natural textiles. The method was originally developed to build up polyelectrolyte multilayers, but recently nanoparticles have also been incorporated in the coatings (Cranston & Gray, 2006; Cranston, Gray, & Rutland, 2010; Decher, Hong, & Schmitt, 1992; Dubas, Kumlangdudsana, & Potiyaraj, 2006; Eronen, Laine, Ruokolainen, & Österberg, 2012; Kotov, Dekany, & Fendler, 1995). The possibility to incorporate various particles and charged molecules opened up new opportunities for the development of functional cellulosic materials. The LbL method has been successfully used on cotton fibres to introduce conductivity, fire retardant and antimicrobial properties (Chen et al., 2016; Gomes et al., 2012; Shirvan, Nejad, & Bashari, 2014). The method has also been used to increase the hydrophobicity of the surfaces, by incorporating low surface energy components, such as petroleum based waxes, into the multilayers (Glinel et al., 2004; Gustafsson et al., 2012). Studies show that the application of carnauba wax dispersions to wood and glass surfaces can greatly increase their hydrophobicity (Bayer et al., 2011; Lozhechnikova, Vahtikari, Hughes, & Österberg, 2015). However, components with opposite charges are required for a successful LbL deposition, while the surfaces of cellulose and carnauba wax particles are both negatively charged. Thus, the poly-L-lysine (PLL) was chosen as a

cationic component of the LbL system in this study. PLL is a highly charged polycation from natural resources and it has been previously utilised to introduce antimicrobial properties to silk and wool fibres (Chang, Zhong, & Xu, 2012; Xing et al., 2015).

Superhydrophobic cellulose-based surfaces would be very interesting for both outdoor applications, such as textile roofs, sun-screen textiles, and sports clothing as well as indoor applications, like domestic textiles (Brown & Stevens, 2007). The common line of the current methods for superhydrophobic textile material production is that they mainly rely on synthetic fibres and/or use synthetic polymers as well as various harmful chemicals for surface hydrophobization. In this work, we introduce a simple and green method to hydrophobize cellulosic substrates, by depositing PLL and wax particles onto the surface. The method is fast and easy to perform, while all materials used are renewable and non-toxic. Furthermore, the LbL treatment is completely water-based and thus can be easily transferred to the modern textile production lines (Brown & Stevens, 2007). To get a better understanding of the layer formation and factors affecting it, quartz crystal microbalance with dissipation (QCM-D) was used to study the build-up process on CNF ultrathin films. QCM-D technique has been previously used to study the LbL build-up of poly-L-lysine with hyaluronic acid (Picart et al., 2001) and heparin (Barrantes, Santos, Sotres, & Arnebrant, 2012). However, to the best of authors' knowledge, no multilayer build-up combining PLL and natural wax particles has been previously reported. The applicability of the method to modification of various cellulosic substrates was demonstrated using CNF freestanding films and commercial cotton and linen fabrics.

2. Experimental

2.1. Materials

2.1.1. Poly-L-lysine

0.1 % (w/v) PLL with a molecular weight of 150,000–300,000 was purchased from Sigma-Aldrich. The pH of the PLL was altered using buffer solutions, 0.1 M HCl and 0.1 M NaOH.

2.1.2. Wax dispersion

Refined carnauba wax was purchased from Sigma-Aldrich. The wax dispersion was prepared by adding wax to hot water at 90 °C and sonicating the mixture for 5 min using Ultrasonic Probe Sonifier S-450 with 1/2" extension (Branson Ultrasonics). Right after sonication, the carnauba dispersion was cooled down in an ice bath, and then filtered through a filter funnel with 100–160 µm nominal maximal pore size. More information about the preparation and characterisation of the wax dispersion can be found elsewhere (Lozhechnikova, Bellanger, Michen, Burgert, & Österberg, 2017). For simplicity, the carnauba wax will be further referred to as wax.

2.1.3. Cellulose nanofibrils freestanding films

A never-dried bleached hardwood kraft pulp was used to prepare the CNF dispersion. No chemical or enzymatic pre-treatment was applied, but the pulp was washed into sodium form (Swerin, Odberg, & Lindström, 1990) prior to disintegration in order to control the counterion type and the ionic strength. The pulp was disintegrated using a high-pressure fluidizer (Microfluidics, M-110Y, Microfluidics Int. Co., Newton, MA). The pulp was circulated 6 and 12 passes through the fluidizer to obtain CNF for self-standing films and QCM-D experiments, respectively.

Freestanding CNF films were used as a substrate to study the performance of the coatings. To prepare a film, 100 mL of 0.85% CNF was filtered through a Sefar Nitex polyamine monofilament open mesh fabric with a 10 µm pore size at 2.5 bar pressure. The film was then hot-pressed in a Carver Laboratory press (Fred S. Carver Inc.) for two hours at 100 °C and with a pressure of 1800 kg/cm². The

Download English Version:

<https://daneshyari.com/en/article/5157416>

Download Persian Version:

<https://daneshyari.com/article/5157416>

[Daneshyari.com](https://daneshyari.com)