Materials and Design 93 (2016) 19–25

Contents lists available at ScienceDirect

Materials and Design

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

Environmental friendly and sustainable gas barrier on porous materials: Nanocellulose coatings prepared using spin- and dip-coating

Martha A. Herrera [a], Juho A. Sirviö [b], Aji P. Mathew [a], Kristiina Oksman [a,b,]*

[a] *Division of Materials Science, Luleå University of Technology, SE-97187 Luleå, Sweden*
[b] *Fibre and Particle Engineering, University of Oulu, P.O. Box 4300, FI-90014 Oulu, Finland*

ARTICLE INFO

Article history:
Received 8 September 2015
Received in revised form 30 November 2015
Accepted 21 December 2015
Available online 24 December 2015

Keywords:
Nanocellulose
Coating
Porous substrate
Oxygen barrier
Microstructure

ABSTRACT

In this study, environmental friendly and sustainable coatings of nanocellulose (NC) were prepared using spin- and dip-coating methods, on two different porous cellulose substrates. Microscopy studies showed that spin-coating technique was suitable for the substrate with smaller pore size, while the dip-coating was suitable for the substrate with larger pore size. The coating thickness ranged from some hundreds of nanometers for the spin-coated layers, to some micrometers for the dip-coated ones. It was also seen that the contact angle increased with the coating thickness and roughness. NC coating resulted in low oxygen permeability (between 0.12 and 24 $\mathrm{mL*\mu m/(m^2*24\,h*kPa)}$) at 23% RH, but at 50% RH the oxygen permeability was too high to be measured, except for the dip-coated sample with 23 μm thickness. Also, it was seen that eight month storing reduced the barrier properties of the coatings when compared with fresh materials. These results indicate that NC coatings have a great potential as sustainable alternative coating on paperboard.

1. Introduction

Nowadays, more than half of the packaging materials used for food and drugs are made of petroleum-based polymers, such as low and high-density polyethylene (LDPE and HDPE). These types of non-biodegradable polymers are selected because of their good gas-barrier properties, mechanical strength and flexibility, along with their low cost and ease of manufacturing, which are crucial properties for packaging applications. However, petroleum-based polymers are associated with high levels of solid residues in land and water bodies (contamination), along with a high dependency on fossil fuel sources. Their poor biodegradability has resulted in increased plastic pollution in oceans from 5.8 million metric tons (MT) in 1975 to 275 MT in 2010, and the prediction for 2025 is one order of magnitude higher, if the current tendency continues [1]. Due to the environmental problems that non-biodegradable packaging materials are causing, interest in the use of biobased materials has increased in recent years. Ideally, the packaging material should be effective in preventing oxygen from penetrating into food, while being environmentally friendly and sustainable [2,3]. To meet these demands nanomaterials, such as clay, have been studied as functional additive to improve gas barrier properties of polymers [4,5]. Also, interest in biopolymers such as poly (lactic acid) [6,7], starch [8] and cellulose acetate [9] has increased during recent years. Apart from polymers, paperboard is a widely used material for packaging applications and has the advantage of being biobased. However, its oxygen transmission rate (OTR) is very high $>400{,}000\ \mathrm{mL*m^{-2}*24\ h^{-1}}$ [10], compared to for example polyethylene 7800–2600 $\mathrm{mL*m^{-2}*24\ h^{-1}}$ [11]. To improve the gas barrier, multilayered structures consisting of paper, polymer or metals are used, but the problem of using non-biodegradable material still exists. Therefore, a biobased coating, such as nanocellulose, could present the ideal solution to improve the barrier properties of paper for packaging applications at low relative humidity (RH), while maintaining biodegradability, sustainability and low gas permeability. Aulin et al. [12] and Lavoine et al. [13,14] showed that coatings of microfibrillated cellulose (MFC) prepared using a simple rod-coating method improved the mechanical properties and the gas barrier of paper. Similar results were obtained by Syverud et al. [15], where MFC coatings, made with a dynamic sheet former, revealed an increase in the tensile index and elongation at break of the coated paper. However, these studies also showed that increasing the RH had a negative effect on the mechanical and barrier properties of the coatings. Nanocellulose coatings can be produced with simple rod-coating or using sheet forming, as mentioned above, but also using a layer-by-layer (LbL) assembly [16–18]. The most common LbL techniques are spin-coating (S-C), and dip-coating (D-C). S-C has proved to be a reliable method for the preparation of reproducible and smooth thin films and the technique is based on the removal of the liquid phase from the material suspension using high-speed spinning. The benefit of the S-C technique is that this method is widely used for the production of very thin coatings (below 10 μm). In S-C, a diluted suspension is placed on the coating substrate and rotated at

---

* Corresponding author at: Division of Materials Science, Luleå University of Technology, SE-97187 Luleå, Sweden.
E-mail address: kristiina.oksman@ltu.se (K. Oksman).

http://dx.doi.org/10.1016/j.matdes.2015.12.127

high speed, while the fluid spins off the edges coating the substrate at the same time that the solvent evaporates [19]. D-C is a method that produces anisotropic coatings on the top of the substrates. The D-C coatings can be as thin as required and this is easily controllable with the concentration of the suspension used. The substrate is immersed into a reservoir of the coating suspension to deposit a layer of material and withdrawn [19].

Coatings of cellulose nanofibers and nanocrystals have shown to decrease the OTR of the coated substrate [12]. However, it is interesting to note that most of the studies are done on self-standing films of cellulose (fibers and/or crystals) or coatings on polymeric substrates [8,9,20–24] but very few on porous substrates such as paper board [12–15,18]. These studies demonstrated how the gas barrier properties of NC coatings improved with the increase in the grammage and density of the coating. Our previous study, about cellulose nanocrystal-coatings on porous substrates, showed that thin films of only 300 nm increased the oxygen permeability of the substrates from completely permeable to values as low as 0.54 $(\text{mL}*\mu\text{m})/(\text{m}^2*24\ \text{h}*\text{kPa})$ [18].

The main goal of this study was to investigate the use of nanosized cellulose as a environmental friendly and sustainable coating on two different porous substrates using S-C and D-C. We investigated how the morphology of the substrates and the coating method affected the thickness, surface characteristics and barrier properties. Additionally, it was of the interest to gain knowledge how the storage time affected the coatings and their barrier properties. Even though there exists some research on microfibrillated cellulose coatings on paper using bar coating method [12–15], the study of coatings of pure nanocellulose on porous substrates using S-C and D-C is a new field of research that is worth investigating. The findings of this study are believed to have a great value, since they support the use of biobased and sustainable materials in packaging applications.

2. Experimental procedure

2.1. Materials and methods

2.1.1. Substrates

Two different porous substrates were used for preparation of the coatings: one with large and the other with small pore size. Substrate (A), was a Whatman cellulose filter paper number 1, with a pore size of 11 μm, and substrate (B) was a Whatman membrane filter mixed cellulose ester, ME25, with a pore size of 0.45 μm. The substrates were cleaned before coating by rinsing three times with the constant addition of acetone and deionized water.

2.1.2. Nanocellulose extraction and analyses

Purified cellulose was obtained from the bioethanol processing route in the pilot-scale plant at SEKAB, Örnsköldsvik, Sweden. The route is described elsewhere [25]. This purified cellulose was dispersed in deionized water (2 wt.%) and homogenized 10 times, using a high-pressure homogenizer (APV 2000, Denmark). A pressure of 500 bars was used to mechanically separate the cellulose particles to nanosize. A single homogenization step took 40 min for a batch of 2 l, resulting in a total time of 400 min. After the homogenization process larger particles and agglomerates were removed using a high-speed centrifuge Avanti™ model J-25I (Palo Alto, USA) with the aim to improve the uniformity of the material size. One liter of homogenized material with 1 wt.% concentration was centrifuged at 6000 rpm for 40 min at 10 °C. The resulting supernatant suspension was collected and named as nanocellulose (NC). The 1 wt.% suspension was used for the coating experiments.

The crystallinity of the NC was measured using PANalytical Empyrean X-ray diffractometer (Almelo, Netherlands). The XRD analysis was made on casted NC films (15 ± 5 μm thickness). The films were exposed to monochromatic CuKα radiation ($\lambda = 1.54$ Å) in the range of $2\theta = 5°–35°$ with step size of 0.02° and a scanning rate of 0.5°/min. The relative crystallinity (C_{Ir}) was calculated using Segal's empirical method and Eq. (1). [26]

$$C_{Ir}\ (\%) = [(I_{200} - I_{am})/I_{200}] * 100\% \tag{1}$$

where I_{200} is the crystalline peak of the maximum intensity at 2θ between 22° and 23°, and I_{am} the minimum intensity for the amorphous cellulose between 18° and 19°. This peak configuration shows the presence of cellulose I [27].

The thermal stability of the NC was studied using thermogravimetric analysis (TGA) Q500 (TA Instruments, New Jersey, USA). The test temperature ranged from 23 °C to 450 °C in air atmosphere, with a heating velocity of 10 °C/min.

Topographical characterization of the NC material was studied using atomic force microscopy (AFM) Nanoscope V, Veeco Instruments (Santa Barbara, CA, USA), using tapping mode at 20 °C and 23% RH. The antimony-doped silica cantilever was oscillated at its fundamental resonance frequency ranging between 320 and 364 kHz, and no image processing, except flattening, was used. A drop of a NC suspension (0.01 wt.%) was placed on a clean mica substrate and left to dry at room temperature. This sample was used to study the morphology and size of the used NC. The average width (height) of the NC was measured from 18 single NC from 3 different height images.

2.2. Preparation of the coatings

Layer-by-layer coatings were performed on the porous substrates (A and B), immediately after being cleaned, using spin-coating (S-C) and dip-coating (D-C) techniques. The used S-C procedure is a modified procedure of the processing presented in our previous study [18]. 1 mL of 1 wt.% NC suspension was placed on the substrate, accelerated at 1260 rpm/s and spun at 3000 rpm for 40 s. Then, the surface was washed three times using 1 mL of deionized water under the same spinning conditions. This defines one layer and this procedure was repeated 5 and 10 times to obtain coatings with 5 and 10 layers, respectively.

The one-face D-C procedure is a modification of the procedure used by Cranston et al. [28]. One face of the substrate was immersed in NC suspension (1 wt.%) for 2 min, after which the sample was completely immersed 3 times in a rinse bath of deionized water in cycles of 10 s. The substrates were then left to dry under ambient conditions for 24 h before the dipping was repeated. This procedure defines one layer and it was repeated until coatings with 5 and 10 layers were prepared. Fig. 1 is a schematic representation of the coating production using S-C and D-C.

The coatings were also stored for 8 months at 25 °C and 42% RH to investigate how the storage time affects the coatings and their gas permeation. Six samples of each material were prepared; three of them were tested directly (within 2 weeks) and three were stored. The prepared coatings and sample coding are presented in Table 1. We will be referring to the non-stored samples unless it is specified that the coatings were stored.

2.3. Characterization of the coatings

2.3.1. Surface morphology

A scanning electron microscope (SEM) JEOL JSM-6460LV (Tokyo, Japan) was used for topographical characterization of the coatings and to measure their thickness from fractured cross-sections. The surfaces and cross-sections of the samples were coated with gold and observed at different magnifications. The thickness values are an average of 20 measurements of 5 different images at different magnifications. The detailed coating network was analyzed using a high-resolution FEG-SEM, Zeiss Merlin (Germany). The samples were coated with tungsten and observed at different magnifications. The surface roughness (Ra) was measured from the AFM images of the coatings. The Ra is the average