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Gas permeability and selectivity of cellulose nanocrystals films (layers) deposited by spin coating

Martha A. Herrera, Aji P. Mathew, Kristiina Oksman*

Division of Materials Science, Luleå University of Technology, SE-97187 Luleå, Sweden

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ABSTRACT

Cellulose nanocrystals (CNC) were extracted from a cellulose residue using two different acid hydrolysis procedures. CNC extracted with sulfuric acid (CNC_S) showed higher surface charge (339 μmol/g) compared with crystals extracted with hydrochloric acid (CNC_{HCl}). Spin-coated films with two different configurations were prepared; the first with alternate layers of poly(allylamine hydrochloride) (PAHCl) and CNC, and the second with a single layer of PAHCl coated with multilayers of CNC. Film characteristics such as roughness, thickness, contact angle, orientation, gas permeability and gas selectivity were studied. Optical microscopy showed more homogeneous films of CNC_S compared to CNC_{HCl}. The surface charge of the crystals impacted the films' hydrophobicity, being highest for 25 alternate layers of PAHCl and CNC_{HCl}. The gas permeability coefficient was different for each film, depending primarily on the surface charge of the crystals and secondly on the film configuration. The films made with CNC_{HCl} displayed gas barriers with nitrogen and oxygen, and gas selectivity with some gas combinations. CNC_S films did not show gas selectivity. These results indicate that CNC with low surface charge can be further developed for gas separation and barrier applications.

1. Introduction

Polymer nanocomposites research has continued to advance since polymer nanocomposites were first prepared in 1990 (Kanatzidis, 1990). Polymer nanocomposites have been shown to have potential application in various sectors such as reinforced materials (Favier, Chanzy, & Cavaille, 1995; Petersson & Oksman, 2006) and gas barrier selectors (Belbekhouche, Bras, Siqueira, Chappey, & Lebrun, 2011), among others. However, due to the increase in the residual problems associated with the use of petroleum-based polymers, the focus in the improvement of polymer nanocomposites is on the use of renewable and natural constituents, like cellulose. Cellulose is a structural polysaccharide found in the cell wall of green plants and some algae (Rånby, Banderet, & Sillén, 1949). This polysaccharide is composed of an amorphous part and a crystalline part known as cellulose nanocrystals (CNC) or nanowhiskers (CNW) (for its rod-like shape). The dimensions of these crystals vary depending on the source from which they are isolated and, in general, CNCs fromwood source have a diameter of around 5 nm and a length of around 200 nm (Belbekhouche et al., 2011; Bondeson, Mathew, & Oksman, 2006; Herrera, Mathew, & Oksman, 2012a). This crystalline cellulose is isolated using acid hydrolysis, which cuts the native cellulose chain, consuming the amorphous part and leaving behind the crystalline part (Rånby et al., 1949). Due to the natural abundance of cellulose, bioinert behavior, low weight, and high strength and stiffness, these nanocrystals have served as an additive in the manufacture of composite materials in recent years (Chen, Liu, Chang, Cao, & Anderson, 2009; Cranston & Gray, 2008; Favier et al., 1995; Gindl & Keckes, 2005). Self-assembly of cellulose nanocrystals has been researched during the last years to obtain films with a high degree of crystal orientation to study the physical properties and crystalline structure of the cellulose (Belbekhouche et al., 2011; Cranston & Gray, 2008; Yoshiharu, Shigenori, Masahisa, & Takeshi, 1997). For a number of studies, the main interest has been the interaction between the crystals on the surface of the cellulosic material and the environment (Belbekhouche et al., 2011; Mohan, Kargl, Doliska, Vesel, & Koestler, 2011; Yoshiharu et al., 1997). For this reason, it is necessary to have a well-defined film with thickness in the nanometric range. Several studies have reported water contact angle and gas permeability properties of cellulose or associated nanocomposites (Belbekhouche et al., 2011; Favier et al., 1995; Kontturi, Johansson, Kontturi, Ahonen, & Thune, 2007; Mohan et al., 2011; Petersson & Oksman, 2006).

* Corresponding author. Tel.: +46 920 493371.
E-mail addresses: martha.herrera@ltu.se (M.A. Herrera), aji.mathew@ltu.se (A.P. Mathew), kristiina.oksman@ltu.se (K. Oksman).

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Petersson and Oksman (2006) compared the barrier properties of polylactide acid (PLA) films reinforced with bentonite or microscrystalline cellulose (MCC) produced by solution casting. It was found that the oxygen permeability was not improved with the addition of MCC, as it was with the addition of the bentonite, which was attributed to lower dispersion of the MCC (Petersson & Oksman, 2006). Belbekhouche et al. (2011) found that solution-casted CNC films were more permeable to gases than films made of microfibrillated cellulose (MFC). This difference was attributed to a higher porosity in the CNC films and their different surface chemistry (Belbekhouche et al., 2011). The wettability of partly, and fully, regenerated cellulose model surfaces from spin-coated trimethylsilyl cellulose was investigated by Mohan et al. (2011). They reported that the wettability of polar and non-polar liquids increased with longer regeneration times. Therefore, it was assumed that the volatile distillation products tend to absorb partly on the regenerated films, which strongly influenced the film's wettability (Mohan et al., 2011). Isotropic films made entirely of CNC using solution casting were shown to perform well in blocking UV light, which makes them suitable in the food packaging industry, where UV protection is required. With the use of solution casting, the resulting films had a thickness of approximately 30 μm (Herrera et al., 2012a).

Spin coating has been shown to be a suitable method of preparing reproducible thin films of cellulose from a solution by removing the solvent with high-speed spinning (Kontturi et al., 2007). The spin coater technique has been used before for the preparation of open, sub-monolayer cellulose films, providing a novel approach for the interpretation of molecular architecture (Kontturi, Thune, Alexeev, & Niemantsverdriet, 2005). Different substrates in the production of CNC thin films have been used to investigate the effect of the substrate on the nanocrystal sub-monolayer (Kontturi et al., 2007). It has been shown that anionic CNC are absorbed on cationic substrates, while anionic CNC cause aggregation on anionic surfaces due to the repulsive forces (Kontturi et al., 2007). Self-assembled multilayered film of cellulose nanocrystals (aionic) and poly(allylamine hydrochloride) (PAHCl) (cationic) have been prepared with the spin coating technique (Cranston & Gray, 2008). Oriented nanocrystals and birefringence that varied with the relative location to the spin axis were found. With this layer-by-layer preparation method, smooth thin films on nanometric scale can be achieved (Aulin, Ahola, Josefsson, Nishino, & Hirose, 2009). These thin films are suitable for many different studies including X-ray diffraction, swelling, contact angle and barrier measurements.

The present work has been done with the objective of comparing two different configurations of spin-coated thin films prepared with CNC extracted from the same raw material source but using different acid hydrolysis methods. The analysis of the physical properties of the films can give insight into the types of applications for which they are best suited. For this reason, CNC surface charge, film appearance, roughness, thickness, orientation, water contact angle, and gas permeability and selectivity were studied.

2. Experimental procedure

2.1. Materials

An industrial residue from dissolving cellulose production (sulfite pulping) was kindly supplied by Domsjö Fabrikerna AB (Örnsköldsvik, Sweden). The residue is filtered from waste water and has a high cellulose content (approx. 96%). The material was received as non-dried cellulose pulp, filtered and with a moisture content of 42%. The residue was used, as received, for extraction of cellulose nanocrystals by acid hydrolysis.

Commercial poly(allylamine hydrochloride) (PAHCl) with a molecular weight of 15,000 g/mol was obtained from Sigma-Aldrich. The PAHCl was used as anchoring layer for CNC in the production of the spin-coated films.

2.2. Acid hydrolysis

Colloidal suspensions of CNC were prepared with sulfuric acid (CNC_S) and hydrochloric acid (CNC_{HCl}). In sulfuric acid (H_2SO_4) hydrolysis, 60 g of cellulose residue was placed in a suspension of 65% H_2SO_4 at 40 °C under mechanical stirring for 30 min, using the procedure developed by Bondeson et al. (2006). The final suspension was concentrated to a concentration of 0.83 wt% cellulose nanocrystals. In hydrochloric acid (HCl) hydrolysis, 50 g of the cellulose residue was placed in a solution of 14.4% of HCl at 80 °C for 225 min, according to a previously reported procedure (Bondeson et al., 2006). The turbid solution was concentrated to a concentration of 0.79 wt% of cellulose nanocrystals. The CNC obtained from both hydrolysis procedures were in form of a colloidal suspension of 1 wt% concentration and the crystals diameters were between 3 and 7 nm, as measured from the height using AFM. The length of the crystals was estimated in our previous study to be between 300 and 500 nm but due to limitations of AFM this is only an approximation (Herrera, Mathew, & Oksman, 2012b).

2.3. Conductometric titration

The surface charge of the crystals was measured using a Metler Toledo SevenEasy™ conductometer and an InLab® 73X sensor (Schwerzenbach, Switzerland). Titration was done to measure the amount of negative charge on the CNC surfaces following a standard route for strong acid versus strong base (Abitbol, Kloser, & Gray, 2013; Araki, Wada, Kuga, & Okana, 1999; Herrera et al., 2012a, 2012b). This method is based on change in conductivity when the charged groups on the CNC surface have been neutralized with NaOH.

2.4. Substrates

2.4.1. Glass

Borosilicate cover glass of $18 \times 18\,mm^2$ and thickness No. 1 (0.16 mm) from VWR International was used. The glass substrates were cleaned with a piranha solution (3:1 concentrated sulfuric acid to hydrogen peroxide) for 30 min and rinsed with fresh deionized water and spin-coated directly.

2.4.2. Filter paper

Whatman ME25 membrane filter (mixed cellulose ester), with a pore size of 0.45 μm, was cut into circles of 25 mm in diameter. The substrates were rinsed three times with the constant addition of acetone and deionized water prior the spin coating.

2.5. Thin film preparation

A Brewer Science Inc. 200X spin coater (Rolla, USA) was used for the deposition of the thin films over the two different substrates. For each substrate two different thin film configurations were made.

In the first configuration alternate layers of PAHCl and CNC were prepared. This procedure is a slightly modified means of polyelectrolyte multilayer film construction used by Cranston & Gray, (2008) and Aulin et al. (2009). Five hundred microliter of a 0.6% PAHCl solution (positively charged polyelectrolyte) 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 1000 μL of deionized water with the same spinning conditions. Thereafter, 500 μL of CNC suspension was added onto the washed layer and