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Carbon dioxide diffusion at different relative humidity through coating of cellulose nanocrystals for food packaging applications

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ABSTRACT

In this paper, the investigation was focused on the CO_2 permeability through CNCs coating at various RH values, comparing with the O_2 one, aiming to evaluate the potential usage in all the applications of modified atmosphere packaging for intermediate-low moisture foods where the role of carbon dioxide is essential for shelf life extension. For this purpose, PET films were coated with characterized CNCs, obtained from cotton linters, and the CO_2 permeance was measured as a function of increasing RH values (from 0% to 80%). After calculating the diffusion and solubility coefficients, and estimating the CO_2/O_2 selectivity, the possible evolution of different modified atmospheres has been theoretically calculated. The results obtained, let hypothesize that, in consequence of a very high CO_2/O_2 permeability selectivity, the CNCs coated films can be useful in some modified atmosphere packaging applications, in a range of RH typical of many medium-high RH food products.

1. Introduction

An intensive research and a general wide interest in the cellulose nanomaterials (CNM) have greatly increased over the last years, up to the point that the "ISO Technical Committee (ISO/TC 229) for Nanotechnologies" recently published a standard vocabulary (ISO, 2017), for cellulose nanomaterials, whose indications are strictly followed in this paper. CNMs are anticipated to have significant commercial impact because for their renewable nature and unique properties. They are believed to have potential applications in a wide range of products including those that currently use non-renewable, oil-based materials or ingredients. In particular, the interest in possible packaging applications of cellulose nano-crystals (CNCs) and cellulose nano-fibrils (CNFs) is continuously and very rapidly growing all around the world (Hubbe et al., 2017; Johansson et al., 2012; Khan, Huq, Khan, Riedl, & Lacroix, 2014; Li, Mascheroni, & Piergiovanni, 2015; Rebouillat & Pla, 2013; Reig, Lopez, Ramos, & Ballester, 2014). In addition to the biodegradability and their origin in renewable sources, there is a strong interest in the potential for activating feasible paradigms of circular economy, related to the chance of producing CNCs and CNFs from cellulose-containing biomasses of food companies or by-products of packaging materials industries.

Actually, very attractive properties can be detected when the size of cellulose molecules is broken down into the nanoscale (Dufresne, 2017). Extraordinary gas barrier functionalities and improved mechanical properties, differently expressed by CNCs and CNFs, lead to very promising applications in bio-based flexible packaging and cellulosic materials for food products. The perspective of optimizing diffusional properties with the purpose of packaging material minimization and possible shelf life extension seems, in particular, a very interesting and current strategy for food packaging innovation, and for high sustainability targets. Several researches have been carried out on the gas barrier properties of cellulose nano-crystals and cellulose nano-fibrils (Aulin, Gallstedt, & Lindstrom, 2010; Gicquel, Martin, Yanez, & Bras, 2017; Minelli et al., 2010; Li, Biagioni, Bollani, Maccagnan, & Piergiovanni, 2013).

In all our previous works, which were carried out on CNCs obtained from different raw materials and coated onto conventional and bio-based films for food packaging, we always found permeance values much lower than those of conventional synthetic barrier layers, even if very thin coatings were applied (less than 1 μm) (Fotie et al., 2017; Li, Biagioni, Finazzi, Tavazzi, & Piergiovanni, 2013; Li, Biagioni, Bollani, 2013; Mascheroni et al., 2016; Rampazzo et al., 2017).

These peculiar and interesting barrier properties of CNCs coatings are not totally surprising, taking into account the main requirements for getting low gas permeability through polymers (Ashley, 1985; Dhoot, Freeman, & Stewart, 2002; McKeen, 2017; Siracusa, 2012; Yam, 2010). In fact, it is well known that highly polar polymers have low gas

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permeability; having high cohesive energy and strong chain-to-chain attractions, their void volume is small and diffusional phenomena are limited (Salame, 1986) at low humidity. Cellulose can be defined a polar polymer since it has many polar oxygen–hydrogen (−OH) groups, with small differences in whatever crystalline forms (Gardiner & Sarko, 1985), even if net dipoles, i.e. a result of opposite charges, are absent.

Un-saturations which lead to a greater ease of chains rotation and consequently to high gas diffusion, are completely absent in cellulose molecules. Short lateral chains which hinder the close packing of macromolecules, increasing free volume and enhancing permeability, as well, are absent in the linear polymers such as cellulose. On the contrary, the crosslinking that restrains the segmental mobility of the polymer and makes the diffusion process slower, is extensively possible due to the crystalline conformation of cellulose, through hydrogen bonds between chains alongside and intramolecular. The crystallinity degree, that in whatever polymer leads to tortuous path in the diffusion pathway of permeants, is always high in cellulose nanocrystals: depending on the different source and preparation process used, the crystallinity index reaches even 80–90% (McKeen, 2017). Finally, the glass transition temperature, which when higher than service temperature is consistent with very stiff chains and gives relatively better barrier properties, is well above 200 °C in the cellulose biopolymers (Fakhraai, Valadkhan, & Forrest, 2005; Gajdoš, Galić, Kurtanjek, & Ciković, 2000).

All that is currently known about morphology and chemical properties of polymers, which positively affect high barrier performance, is noticeable in cellulose and, particularly in cellulose nano-crystals.

At the same time, however, it has been noted that the lack of intramolecular hydrogen bonding in the surface chains of cellulose makes possible extensive interactions with water molecules. Various studies dealing with these kind of phenomena, showed that the water content and interactions with the material's components have a great influence on final properties of cellulosic materials (Engelund, Thygesen, Svensson, & Hill, 2013; Froix & Nelson, 1975; Ioelovich & Leykin, 2010). For more than 70 years, bulk amorphous regions have been indicated to be an ideal place for water adsorption, and the relationship between the availability of surface hydroxyl groups and crystallinity of cellulose is well established (Howsmon, 1949; Mihranyan, Llagostera, Karmhag, Strømme, & Ek, 2004).

The moisture sensitivity is a serious critical point for preserving the outstanding gas barrier properties of CNCs coatings, particularly if they are expected to be used in food packaging applications. Actually, we always observed a strong reduction of oxygen barrier properties at medium-high relative humidity values (Fotie et al., 2017; Rampazzo et al., 2017) and recently (Fotie et al., 2017), by a multidisciplinary approach, we tried to better understand the basics and the entity of water-cellulose nanocrystals interaction. Starting from about 40% of equilibrium relative humidity (RH), we assessed a 65% of freezable water in the CNCs and the XRPD (X-Ray Powder Diffraction) patterns gave clear indications of loss of structural coherence in the increasing of the RH values, and that the amorphous regions in the sample expanded at the expense of the crystalline part.

In this paper, the investigation was continued and focused on both the O_2 and CO_2 permeability of CNCs coatings at various relative humidity values. A potential application for such a high barrier material is in fact, the modified atmosphere packaging of food products, where the role of carbon dioxide is essential for shelf life extension of perishable foods which have medium or high relative humidity values.

2. Materials and methods

2.1. Materials

The cotton linters used for CNCs production were obtained from Innovhub (Milan, Italy), the chemical reagents were purchased from Sigma-Aldrich (Milan, Italy) and the 12 μm thick polyethylene terephthalate (PET) film, used as coating substrate, was achieved by Sapici spa (Cernusco sul Naviglio, Italy).

2.2. CNCs obtainment and coating deposition

The Leung and co-workers method was followed for the CNCs preparation, throughout the oxidative hydrolysis process by ammonium persulfate (APS) 1 M, in the ratio APS (cm^3)/cotton linters (g) 100:1 (Leung et al., 2011). The yield of CNCs production (%) was calculated as the ratio of freeze-dried CNCs weight (g) and cellulosic content of 100 g of raw materials. The steps of CNCs purification and the coating application on PET films, were followed as described in previous works (Mascheroni et al., 2016; Rampazzo et al., 2017); the coating suspension was a CNCs 4% (m/m), adjusted at pH 8 with NaOH 1 M. For the thickness assessment of CNCs coating, a gravimetric method was used. After weighing 4 samples (M1, g) of 100 cm^2, the coating was washed out under hot water (~70 °C) and the resulting uncoated PET films were dried and weighed (M2, g). The coating thickness (L, cm) was estimated by Eq. (1):

$$L = (M1\text{-}M2)/(\rho \times 100) \quad (1)$$

where $\rho = 1.58\ g\ cm^{-3}$ is assumed as the density of the CNCs (Mazeau & Heux, 2003).

2.3. Characterization of CNCs morphology and coating uniformity

Either equivalent hydrodynamic diameters of the dispersed CNCs, and particle number distributions were determined by dynamic light scattering (DLS) measurements (mod. Litesizer500, Anton Paar, Graz, Austria). The measurements were performed at 25.0 ± 0.1 °C with a 35 mW laser diode light (λ = 658 nm) and collecting the scattered light at 15°and 90°. Prior to proceeding with the measurements, the samples were diluted at 3 different concentrations with distilled water adjusted to pH 8 and maintained at 25 °C through stirring until measurement. The diluted solutions were flowed in the measurement cell after 30 s homogenization by ultrasonic (UP 200 St, Hielscher ultrasonics GMBH, Teltow, Germany) in a cool water bath to prevent overheating. The dimensions of the CNCs were next evaluated via Transmission Electron Microscopy (TEM). Drops of aqueous dispersions of CNCs (1%) were settled on carbon-coated electron microscope grids, negatively stained with uranyl acetate and left to dry. Samples were analysed with a Hitachi Jeol-10084 TEM operated (Brugherio, Italy) at an accelerating voltage of 80 kV.

Surface structure of the PET coated films was also evaluated by Atomic Force Microscope. Three different samples were measured with Tosca™400 AFM (Anton Paar, Graz, Austria) in tapping mode. Three randomly selected positions were measured for each sample. All images were recorded with the same scan size of 5 x 5 μm and resolution 500 × 500. Surface roughness (Sq, root mean square) has been calculated from AFM images following standard procedure (ISO, 2012). The transparency of the CNCs coated PET was also measured at 550 nm, according to the ASTM D 1746-70, by means of a UV-VIS spectrophotometer (mod. L650, Perkin-Elmer, Milano, Italy). Each sample was replicated three times, analyzing at least four spots on each replicate.

2.4. CNCs zeta potential and conductivity

Zeta potential (mV) and conductivity (mS cm^{-1}) of the CNCs in the diluted suspension at 3 different concentrations at pH 8 were performed by electrophoretic light scattering (ELS), using the PALS technology (mod. Litesizer 500, Anton Paar, Graz, Austria). Measures were replicated 5 times, at 25.0 ± 0.1 °C, by means of a 35 mW diode laser (λ = 658 nm) and at 15° detection angle.

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