Food Packaging and Shelf Life xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Food Packaging and Shelf Life

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

Cellulose nanofibrils/nanoclay hybrid composite as a paper coating: Effects of spray time, nanoclay content and corona discharge on barrier and mechanical properties of the coated papers

Seyedmohammad Mirmehdi[a,*], Paulo Ricardo Gherardi Hein[a], Claire Isabel Grígoli de Luca Sarantópoulos[b], Marali Vilela Dias[c], Gustavo Henrique Denzin Tonoli[a]

[a] Departamento de Ciências Florestais, Universidade Federal de Lavras, Cx P. 3037, 37200-000, Lavras, MG, Brazil
[b] Instituto de Tecnologia de Alimentos, Universidade Estadual de Campinas, CEP 13070-178, São Paulo, SP, Brazil
[c] Departamento de Ciência dos Alimentos, Universidade Federal de Lavras, Cx P. 3037, 37200-000, Lavras, MG, Brazil

ARTICLE INFO

Keywords:
Cellulose nanofibrils
Nanoclay
Spray coating
Barrier properties
Corona discharge

ABSTRACT

The objective of this paper was evaluate the effects of spray time, nanoclay content and corona discharge on oxygen transmission rate (OTR), water vapor transmission rate (WVTR), basis weight, thickness and tensile strength of the coated papers. An aqueous slurry base, a mixture of cellulose nanofibrils (CNF) and nanoclay particles, was sprayed on a kraft writing & printing paper surface as base substrate. Upon drying, the suspension on the paper surface formed a hybrid nanocomposite layer with CNF (matrix) and nanoclay (mineral filler). Paper substrate was coated by a laboratory-assembled spray coater. Corona discharge enhanced the wetting of paper surfaces, improving adherence between paper and hybrid composite. Increased spray time improved tensile strength and barrier properties i.e. OTR and WVTR. Higher nanoclay content in coated paper enhanced its barrier properties but reduced its tensile strength. Tensile strength and morphological properties demonstrated effective adhesion between base substrate and hybrid composite.

1. Introduction

The leading concern in developing and producing multilayer composites for food packaging are suitable barrier and mechanical properties and obviously interfacial adhesion between the coating layer and the base substrate (Langhe & Ponting, 2016). Cellulose nanofibrils (CNFs) are aggregations of rudimentary nanofibrils with micrometer length and 10–100 nm in diameter (Jonoobi et al., 2015). In low concentrations (of around 2%), CNFs form a gel-like substance, useable in producing biodegradable, homogenous and dense films (Vartiainen & Vikman, 2013; Vartiainen, Pöhler, & Sirola, 2011).

The primary application for these fibers is the production of paper and packaging materials. Perhaps an explosion in new green materials and biopolymers is about to occur, but at the time of this writing, paper and paperboard are the sole renewable materials extensively employed in packaging applications.

Numerous studies (Chinnama et al., 2016; Beneventi et al., 2014; Hult, Iotti, & Lenes, 2010; Missoum, Martoïa, Belgacem, & Bras, 2013) have been conducted with the objective of creating cellulose packaging materials with enhanced mechanical and barrier properties, and promising results have been realized.

Biopolymers possess intrinsic permeability to vapors and gases, with poor mechanical properties, boosting interest in discovering new strategies to improve such properties (Majeed et al., 2013). With cheap, renewable and sustainable materials featuring enhanced barrier and mechanical properties, food packaging materials are expected to expand (Ghaderi, Mousavia, Yousefi, & Labbafi, 2014). Nanoclay-nanocellulose composites have emerged lately as a new type of composite material, with interesting strength and gas barrier properties (Kalia, 2016). These organic-inorganic hybrid composites are environmentally friendly, and obtainable from renewable resources (Wu, Yang, Takeuchi, Saito, & Isogai, 2014). In food packaging applications, these composites will soon pose a meaningful alternative to biopolymers or polymer-inorganic composites (Gamelas & Ferraz, 2015). Nanoclay hydrophilic bentonite with formula $H_2Al_2O_6Si$ are naturally aluminum silicate, composed of fine-grained minerals having sheet-like geometry referred to as phyllosilicates (Wu et al., 2014). Industrial applications for nanoclays include multilayer film packaging and thermoform

* Corresponding author.
E-mail address: mohamadmirmehdi@yahoo.com (S. Mirmehdi).

https://doi.org/10.1016/j.fpsl.2017.11.007
Received 15 May 2017; Received in revised form 9 October 2017; Accepted 28 November 2017

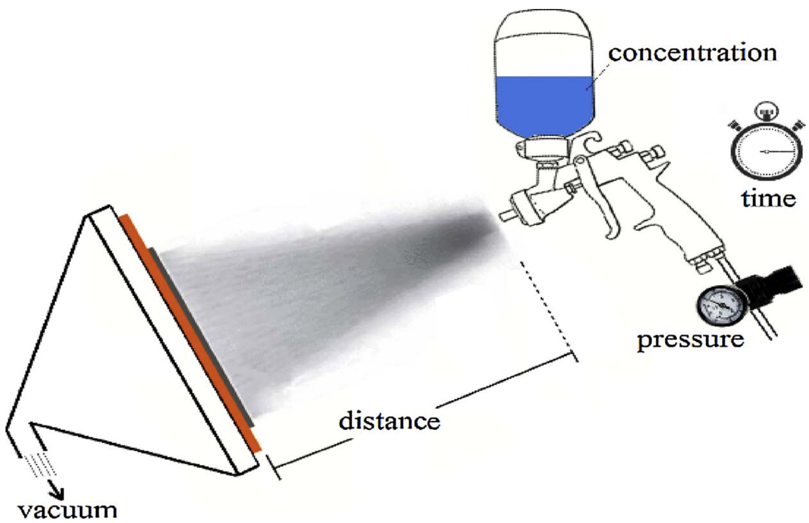

Fig. 1. Scheme of the experimental procedure used to coat the P&W paper substrates.

containers in which reduce gas permeability and keep oxygen-sensitive foods fresher and thus increase the shelf life of the foods (Silvestre, Duraccio, & Cimmino, 2011).

Among the several coating methods to produce multilayer composites, spray coating has many advantages. Since the coating is carried out contactless, a contour coat maybe applied to uneven surfaces. The substrate's topography has no bearing on coating weight. Tear-sensitive web material can be coated. Low coating weights are achievable at high web velocities. Closed film can be attained with less liquid, leading to improved cost and higher quality (Czerwonatis, 2008).

For improvement adherence between layers in multilayer packaging, variety of methods and surface treatments like electroplating, chemical process, anodic oxidation, thermal spraying and etc. are used to improve functionality of surfaces, mainly to increase wettability and adhesion. Corona is a visible electrical discharge which occurs when a high voltage, high frequency electrical potential is applied to a surface and increases the surface energy and consequently, the adhesion of the solid material surfaces which is called surface wetting. A material is considered wetted if its surface energy is greater than the liquid's surface tension. Corona discharge is often found in coating, printing and laminating of plastics, cloth, and paper (Butt, Graf, & Kappl, 2013). Corona discharge on the base substrate, improves adhesion in spray coating method and in barrier properties in packaging materials (Pykönen et al., 2008).

In this research, a coating layer of a hybrid composite of nanoclay and cellulose nanofibrils on paper substrate is proposed as a nanotechnology for environmentally compatible food packaging materials. An aqueous slurry water base suspension of CNF/nanoclay was sprayed on the paper's surface using a laboratory-assembled spray system. Some papers were treated using corona discharge to evaluate adherence and improved features by generating both a denser layer and more adhesion. The barrier properties (oxygen transmission rate and water vapor transmission rate), tensile strength, and physical properties (thickness and basis weight of the coated paper) were examined.

2. Materials and methods

2.1. Materials

Paper substrate was a commercial printing & writing (P&W) paper supplied by SuzanoPapel e Celulose, Brazil, made of 100% cellulose of Eucalyptus with a basis weight of 75 g/m^2 and a thickness of 95.5 µm. To prepare the CNF, bleached dry lap *Eucalyptus* Kraft pulp was obtained from a commercial source (Cellulose Nipo-brasileira – Cenibra, Brazil). Nanoclay hydrophilic bentonite (Sigma-Aldrich) with formula $H_2Al_2O_6Si$ with average particle size ≤ 25 µm, was used as a filer in the matrix of cellulose nanofibrils.

2.2. Methods

2.2.1. Obtaining the cellulose nanofibrils (CNF)

The pulp was first soaked in deionized water overnight and then disintegrated in a lab mechanical stirrer (Fisatom, model 722). The Eucalyptus pulp was fibrillated at suspension solids consistency of 1% (w/w) using a Supermasscolloider (Model: MKCA6-2J, Masuko Sangyo Co., Ltd, Japan) at 1500 rpm and the suspension was passed through it 30 times following suggestions of previous works (Bufalino, Neto, & Rodrigues, 2015; Fonseca, Raabe, & Sartori, 2015; Piva, Fonseca, & Costa, 2013; Tonoli, Holtman, Gregory, & Fonseca, 2016).

2.2.2. Morphology of fibers and nanofibrils

A Leica DM4000 B compound light optical microscope (OM) was used for the initial investigation of the morphology of the pulp fibers and also of obtained cellulose nanofibrils. Suspensions were stained with a drop of ethanol–safranin solution (0.5% v/v) in order to increase the contrast between phases. The obtained cellulose nanofibrils were also viewed in a transmission electron microscope (TEM) FEI Tecnai 12 operated at 120 kV. A drop of the suspension was deposited on a formvar/carbon coated 400 mesh copper grid, and dried before viewing with TEM. The average diameter of the micro/nanofibrils was determined by digital image analyses (Image J 1.48 v, National Institutes of Health, USA). A minimum of 500 measurements was collected for data analysis.

2.2.3. Corona discharge

The treatment with corona discharge was done using of a continuous electrical discharger (Corona Brasil Ind., model Pt-1) of high voltage, i.e. 10 kV, frequency of 60 Hz, potential of 0.5 kW and electric current of 0.06 A, which can increases the surface wettability of paper before coating, and allowing the improved adherence of other materials (Davis and Badu-Tawiah, 2017). Paper sheets were passed with 1 cm distance under the tip of the stationary electrode at a speed of 450 mm/min.

2.2.4. Spray coating of paper

CNF/nanoclay suspension was spray coated onto P&W paper substrates using a lab spray coater (see Fig. 1). Variable parameters of spray were selected regarding to the best treatment of our previous study (concentration of CNF 1.4%, pressure of spray 5 bar, and distance of spray 15 cm).