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Nanocellulose-polypyrrole-coated paperboard for food packaging application

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ABSTRACT

Currently, studies on packaging that improves the shelf life of perishable food while reducing the waste that is produced upon disposal are encouraged. Thus, exploration of the property improvement of paperboard (Pb) packaging is of interest since this type of packaging is biodegradable and recyclable. This work emphasizes the added value of (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO) oxidized cellulose nanofibres (TOCN) and polypyrrole (PPy) coating on such paperboard. The mechanical properties and reduced gas permeability of the coated paperboard (CPb) were significantly improved due to the dense network formed by TOCN and polypyrrole particles. These results suggest that surface coating by polypyrrole particles may be utilized for the manufacture of multilayer paperboard containers in industrial applications to reduce packaging waste generated by the often added conventional plastic.

1. Introduction

Food packaging must provide sufficient protection to ensure food quality and safety. Thus, the selection of packaging materials is of crucial importance in the food market. These materials need to withstand environmental factors, such as temperature and relative humidity, that may affect their properties such as their barrier or permeability characteristics [1]. Moreover, the food industry, which is one of the largest users of packaging, also wants to use the minimal amount of raw materials to reduce their production costs [2].

In response to the growing expectations of our society, works on nanotechnology applications in packaging have attracted significant attention in recent years [3–5]. These materials can offer better food quality preservation and product security by slowing and preventing microbial development [6,7]. In particular, the use of active packaging of antibacterial type aims to reduce or inhibit the growth of bacteria that could develop on food [1,7]. Synthetic polymer materials, such as polyethylene, have been widely used as food packaging because they are easy to process, present good gas or grease barrier properties and are adaptable. However, these packaging materials, which are almost always non-degradable, have generated great waste pollution [8]. Therefore, the increasing concerns about environmental impacts and fossil material availability have led to the need for new packaging materials. Currently, substantial efforts are ongoing to find alternative packaging that could still extend the food shelf life and quality while reducing packaging waste [9]. In this matter, the industry is seeking solutions with biodegradable packaging from renewable resources, as their use could solve the waste problem to some extent [1,10].

Thereby, cellulosic materials such as paper or paperboard are increasingly used as food-packaging materials. However, like their synthetic polymer counterpart, bio-based packaging must have the same functions, such as protection, quality preservation and food safety [7]. Unfortunately, the use of these materials is strongly limited because of their susceptibility to humidity and weak mechanical properties [11]. Thus, numerous solutions have been explored to improve the properties of bio-based packaging, such as the blending of these materials with synthetic polymers, chemical modification or a simple coating. Great attention has recently emerged around the use of protective coatings on paperboards for food packaging [10]. This solution allows the product quality and freshness to be kept over time, as required for its commercialization until its consumption [5,12]. Ideally, this layer can also be used as a barrier against organic solvents (increase in the hydrophobicity) or to decrease the water vapour transmission rate and oxygen permeability of paper and paperboard [13], but some challenges would result from this approach. Moreover, the dispersion coating has the advantage of being an efficient and fast pace production process. This process allows the use of mono or multilayer structures of the coated paperboard, with acceptable properties for food packaging,

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and this process can lead to a more compostable product if it has the right kind of coating [14,15].

Thus, the use of biopolymers, as dispersion coating, is increasing, especially the use of cellulosic fibres (nanocellulose or microfibres), which are biodegradable and recyclable [5,16]. Moreover, cellulose nanofibres have even demonstrated good resistance to oxygen in addition to their excellent mechanical properties due to the creation of a tight network [17–19]. Nonetheless, the high water affinity of cellulose is an important inconvenience for some packaging. Blends of biopolymers or synthetic polymers can solve this problem. Polypyrrole (PPy) coupled with cellulosic material has demonstrated an increase in the hydrophobic character and a decrease of the water vapour transmission rate (WVTR) [20]. The PPy coating on cellulosic materials was found as a very interesting alternative to preserve food quality and safety because it exhibits complementary attractive properties such as antibacterial and antioxidant properties [21–23].

The goal of this study is to prepare a coated paperboard with TOCN and polypyrrole as a food packaging medium. This coating should combine the biodegradability, the mechanical properties and low gas permeability of the nanocellulose with the physico-chemical properties of PPy. If successful, the multilayer composite appears to be an excellent candidate for active food packaging.

2. Materials and methods

2.1. Materials

Pyrrole (C_4H_5N) and iron (III) chloride ($FeCl_3$) were purchased from Sigma Aldrich and used as received. The TOCN gel was produced through the TEMPO oxidation and sonication treatments of bleached Kraft wood pulp [24]. This gel is composed of 30% long fibres (micro) and 70% short fibres (nanofibres) with an average width and length of approximately 3.5 ± 1.0 nm and 306 ± 112 nm, respectively [25]. Moreover, the carboxyl rate was evaluated according to [24] as 1480 ± 40 mmol/kg. A commercial unbleached flat paperboard (Pb) with a thickness of 50 µm and grammage of 45 g/m^2 was used.

2.2. Methods

2.2.1. Coating process

As the first step, 2 ml of a pyrrole solution (98%) was added to 80 ml of TOCN suspension (0.5% w/w). The mixture was then stirred for 10 min, and 10 ml of a 0.3 M oxidant solution ($FeCl_3$) was added to initiate the polymerization of pyrrole into polypyrrole (Fig. 1). The mixture was kept under stirring for 30 min before turning black, showing signs of pyrrole polymerization. Afterwards, the TOCN-PPy mixture was rinsed with demineralized water before it was cast on the paperboard. Then, the coated paperboard (CPb) was dried under ambient air before it was calendered three times at room temperature and 200 Psi (1.3 MPa) to obtain a flat paperboard.

Table 1
Grammage (g/m^2) and thickness (µm) of each paperboard.

	Grammage (g/m^2)	Thickness (µm)
Paperboard	45.5 ± 0.9	501.0 ± 2.0
Coated Paperboard	49.0 ± 0.7	520.0 ± 7.0

2.2.2. Structural characterization of paperboards

Before characterizations, the samples were conditioned at room temperature and a relative humidity (RH) of 50% for 24 h. The weight was determined as an average value of the Pb and CPb by measuring at least six samples, with the precision of ± 0.001 g. According to the standard ISO 534:2011, the thickness was measured with a Lhomargy micrometre (± 0.01 mm) and was determined by six measurements from Pb and CPb. These values were also checked by cross-sectional (obtained by a microtome) scanning electron microscopy (SEM) images of our samples using a VP-SEM SU 1510 (Hitachi, Japan). Additionally, the morphology of the paperboards was obtained using this SEM equipped with energy-dispersive X-ray spectroscopy (EDX) analysis from Oxford Instruments (United Kingdom). The samples were gold-coated using an International Scientific Instrument PS-2 coating unit (India). Attenuated Total Reflectance - Fourier Transform Infrared Spectroscopy (ATR-FTIR) spectra were obtained at room temperature on a Nicolet IS10 FT-IR spectrometer (ThermoScientific, USA). Each spectrum was acquired in the range of 3600–600 cm^{-1} from 16 scans with a resolution of 4 cm^{-1}. Duplicates of each sample were realized at three different points.

2.2.3. Paperboards properties characterization

The air permeability of the samples was measured by a Parker Print Surf instrument, according to the standard ISO 5636:3. The airflow that passes through the sample for a known surface area, when clamped between two measuring rings at a tightening pressure of 1960 kPa, is expressed in ml/min. Tensile strength of the paperboards was measured at 10 mm/min extension speed on a universal testing machine (Instron 4201) at room temperature and controlled humidity. Young's modulus was determined from the stress–strain curves. The samples used in these measurements were cut from the coated paperboard and paperboard to length of 25 mm, width of 3 mm and thickness in the range of approximately 0.05 mm. The average value of five replicates for each paperboard was collected. Static contact angles were determined by a FTA4000 contact angle measuring system (First Ten Angstroms). At least 5 drops (approximately 3.10^{-2}µl in volume) of distilled water were deposited onto each paperboard and a total of 300 images were captured within 90 s for each drop.

2.2.4. Food packaging simulation

A simulation with cherry tomatoes was performed to determine if the CPb presents any advantage for use as food packaging. Small boxes from paperboard and coated paperboard were prepared. Since future box could need to be printed, which the final black colour prevent

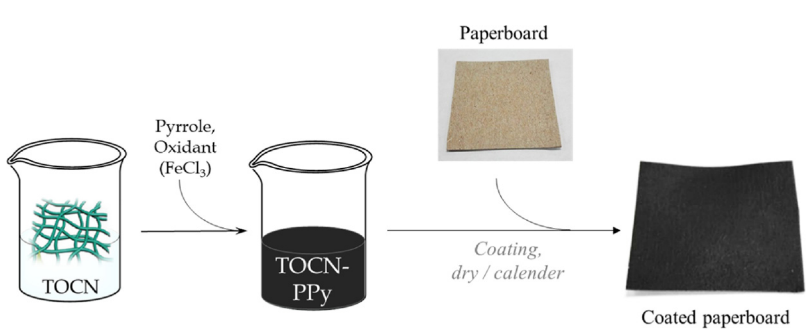

Fig. 1. Schematic illustration of the coating of paperboard by TOCN/PPy.