

# Polypyrrole/nanocellulose composite for food preservation: Barrier and antioxidant characterization

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## ABSTRACT

When food cannot be consumed immediately after production, food packaging must create a protective atmosphere around the food product. The packaging must improve the shelf life of perishable foods and protect the food from dirt, dust, oxygen, light, pathogenic microorganisms, and moisture by acting as an effective barrier to moisture, gases (CO<sub>2</sub> and O<sub>2</sub>) or even by possessing antimicrobial properties. However, extending the shelf life and enhancing food quality while reducing packaging waste is encouraged. The exploration of new bio-based packaging materials, such as TEMPO-oxidize nanofibrillated cellulose (TOCN), has increased due to its biodegradable and renewable character. This work emphasizes the antioxidant activity and high barrier properties against the diffusion of oxygen, carbon dioxide and water vapor from a nanocomposite based on polypyrrole (PPy) and TOCN, as well as its biodegradability for food packaging applications. The preparation, characterization and application of the nanocomposite in food packaging are discussed.

## Graphical abstract

**Keywords:** polypyrrole; nanofibrillated cellulose; gas barrier; antioxidant; composite

## 1. INTRODUCTION

Nanotechnology matches the utilization of nanostructures, which confers matchless properties and functions for new applications. A new generation of food packaging, based on nanomaterials, has attracted much attention in recent years and represent a better alternative, in response to conventional food packaging (Huang & Zhou, 2012; Cushen, Kerry, Morris, Cruz-Romero & Cummins, 2012; Sorrentino, Gorrasi & Vittoria, 2007). In fact, the advent of nanotechnology offered new prospects for the conception of innovative food packaging required by industrial requirements. These new materials can be the key for maintaining food quality, freshness and product security to slow and to prevent microbial development and the associated physiological and chemical changes in food produced by microbial and enzymatic activity (Bradley, Castle & Chaudhry, 2011; Lavoine, Desloges, Manship & Bras, 2015).

Microbial and enzymatic activities are not the only responsible party for most of the degradation reactions of foodstuffs. Oxygen, either directly or indirectly, plays an important role in the losses of organoleptic and nutritional properties as well as food spoilage by aerobic microorganisms. For example, maintaining a low

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46 oxygen environment is essential to extend the life of meat (Brandon, Beggan, Allen & Butler, 2009). It is therefore  
47 necessary to use materials with good oxygen barrier properties (Duncan, 2011). However, residual oxygen  
48 levels that are sufficiently high promote food spoilage. To address this problem, oxygen scavengers or  
49 antioxidants may be incorporated (Busolo & Lagaron, 2015). The presence of antioxidants may reduce the  
50 oxidation kinetics, even in the presence of oxygen. For this reason, the food industry has shown increasing  
51 interest in the development of active packaging with antioxidant properties which can be incorporated into  
52 mono or multilayer structures, or coated on the packaging layer (Arrua, Strumia & Nazareno, 2010; Brody, 2001).

53 However, the increased use of plastic packaging will become a scourge for nature (Kirwan & Strawbridge,  
54 2003). In this regard, industry is seeking solutions with bio-based products for the new generation of food  
55 packaging. Among these new solutions, cellulose has been widely explored since it can confer  
56 biodegradability, a recyclable character for packaging (Sorrentino et al.; Lavoine, Desloges & Bras, 2014). Cellulose  
57 nanofibers have even demonstrated barrier properties to oxygen in addition to its excellent mechanical  
58 properties due to the fibers that are mostly entangled and are form a tight network (Nair, Zhu, Deng &  
59 Ragauskas, 2014; Lavoine, Desloges, Dufresne & Bras, 2012). Nevertheless, cellulose has a major inconvenience for  
60 packaging, its affinity for water. Indeed, cellulose films have very poor barrier properties to water vapor  
61 because of its hydrophilicity. To resolve this problem, we have coupled TOCN (nanofibers obtained by  
62 TEMPO oxidation) with a semi-conductive polymer, polypyrrole and polyvinyl alcohol (PVA). The PPy  
63 coating was an interesting alternative due to its hydrophobic character. Moreover, PPy confers attractive  
64 properties for its active packaging as antibacterial and antioxidant properties. In addition, the PVA chains  
65 allow better tensile strength. The goal was to prepare a packaging that simultaneously combines the  
66 biodegradability and the barrier properties to gas of cellulose with the physico-chemical properties of PPy.  
67 This composite appears to be an excellent candidate for active food packaging in response to the demands  
68 of the food industry.

## 69 **2. MATERIALS AND METHODS**

### 70 **2.1. Materials**

71 All chemicals (Pyrrole ( $C_4H_5N$ ), iron (III) chloride ( $FeCl_3$ ), PVA (Mw 146,000–186,000, 98–99%  
72 hydrolyzed) were purchased from Sigma Aldrich. The TOCN gel was produced through the TEMPO  
73 oxidation and sonication treatments of bleached Kraft wood pulp at a concentration of 2.5 wt %. 4-  
74 acetamido-(2,2,6,6-Tetramethylpiperidinyloxy) is a stable nitroxyl radical, which is used to catalyze the  
75 oxidation reaction. It was observed that the use of ultrasound with this TEMPO oxidation reduces the  
76 quantity of the reagent, increases the carboxylate rate ( $\sim 3\%$ ) and increases the TOCN ratio (Mishra, Manent,  
77 Chabot & Daneault, 2012). The TOCN gel that was used is composed of micro and nanofibers. The ratio was  
78 estimated to 30% of long and 70% of short fibers with an average width and length of approximately  $3.5 \pm$   
79  $1.0$  nm and  $306 \pm 112$  nm, respectively (Rattaz, Mishra, Chabot & Daneault, 2011). The carboxyl rate and degree of  
80 polymerization were evaluated to be 1600 mmol/kg and 200, respectively.

### 81 **2.2. Methods**

#### 82 **2.2.1. Coating process**

83 To begin, a small quantity of PVA solution (0.08 g in 2 ml of water) was added to 50 ml of TOCN  
84 suspension at a concentration of 0.5%. The mixture was stirred at a moderate speed and at room  
85 temperature to prevent bubble formation, and the resulting solution was poured into an aluminum dish. The  
86 film was oven dried for three days at ambient conditions. Then, the TOCN/PVA film was soaked in an  
87 oxidizing solution of 0.2 M  $FeCl_3$  for 30 min, before adding 2 ml of pyrrole, which was distributed over the  
88 entire film. After 30 min of polymerization, the film became dark and was coated with PPy chains. The  
89 composite was thoroughly rinsed with distilled water to eliminate all the residues and dried between two  
90 hot plates at 95°C. In comparison, we prepared TOCN films from suspension at a concentration of 0.5%.

#### 91 **2.2.2. Structural characterization of composite**

92  
93 Before the tests, the of the samples were conserved at room temperature and a relative humidity (RH) of  
94 50% for 24 h. The weight was determined as an average value of the samples by measuring at least ten  
95

96 circular samples of 8.2 cm in diameter, with the precision of  $\pm 0.001$  g. According to the standard ISO  
97 534:2011, the average thickness of each sample was measured with a Lhomargy micrometer ( $\pm 0.01$  mm)  
98 and was determined by five measurements from all the samples and is reported in Table 1. The mean value  
99 and standard deviation were calculated from both the weight and thickness measurements. These values  
100 have also been checked by cross sectional (obtained by a microtome) scanning electron microscopy (SEM)  
101 images of the samples with a JEOL JSM T300. The NFC/PVA samples were coated with gold using an  
102 Instrumental Scientific Instrument PS-2 coating unit. ATR - Fourier Transform Infrared Spectroscopy  
103 (FTIR) spectra were obtained at room temperature on a Nicolet IS10 FT-IR spectrometer  
104 (ThermoScientific). Each spectrum was acquired in the range of  $600\text{--}4000\text{ cm}^{-1}$  from 16 scans with a  
105 resolution of  $4\text{ cm}^{-1}$ . Duplicates of each sample were analyzed at five different points. Atomic force  
106 microscope (AFM) observations were performed with an MFP-3D-SA (Asylum Research, Inc.) in tapping  
107 mode, under ambient conditions. Roughness was measured with a measurement point density of up to 100  
108 million measurement points by an optical microscope (Infinite Focus) with a 3D system based on Focus-  
109 Variation.

110  
111 *Table 1: Grammage ( $\text{g}/\text{m}^2$ ), thickness ( $\mu\text{m}$ ) and specific gravity of each film.*

112

### 113 **2.2.3. Composite barrier properties characterization**

114 **Water permeability.** The measurements were carried out in accordance with the standard TAPPI, 2014,  
115 «water vapor transmission rate of paper and paperboard at  $23^\circ\text{C}$  and 50% RH», norm T 448 om-04. This  
116 method provides for gravimetric determination of the water vapor transmission rate (WVTR) of materials at  
117  $23^\circ\text{C}$  with an atmosphere of 50% RH and gives the WVTR in  $\text{g}/\text{m}^2/\text{day}$ . Measurements on the samples area  
118 of  $30\text{ cm}^2$  were collected for 5 days with readings taken twice a day. The film thickness was used to  
119 normalize the values within the software of the apparatus.

120

$$121 \text{WVTR} = 24 x / A y$$

122

123 where x is the mass gain in grams over the time period y; y is the time in hours for the gain x; and A is the  
124 exposed area of the specimens in  $\text{m}^2$ .

125

126 **Air permeability.** The air permeability of the TOCN, TOCN/PVA and TOCN/PVA-PPy samples were  
127 measured with a Mariotte vase, according to the standard ISO 5636. The measurements were performed on  
128 samples with an area of  $9.6\text{ cm}^2$ , under ambient air conditions, with a vacuum of 2.5 kPa. The volume of  
129 water that flows in the catch tank is collected after 10 min and the average air permeability was then  
130 calculated from at least three measurements. Our films have a very low air permeability so the values have  
131 been compared to the air permeability of paper sheets alone to demonstrate the barrier properties.

132

$$133 I_p = V/A t \Delta P$$

134

135 with  $I_p$  being the index of permeability; V is the volume in  $\text{cm}^3$ ; A is the area in  $\text{m}^2$ ; t is the time in seconds;  
136 and  $\Delta P$  is the change in pressure in Pa.

137

138 **Oxygen permeability.** The oxygen permeability was monitored at  $23^\circ\text{C}$  and 85% RH using an oxygen  
139 permeation analyzer (model M8001, Illinois Instruments, Inc. US). The test was performed according to the  
140 standard ISO 15105-2:2003. The analysis was performed in duplicate for the TOCN, TOCN/PVA,  
141 TOCN/PVA/PPy samples over an area of  $5,31\text{ cm}^2$ . The film thickness was used to normalize the values  
142 within the control software. The measurement of the oxygen transmission rate (OTR) of the samples was  
143 determined in  $\text{cm}^3/\text{m}^2.\text{day}$ .

144

### 145 **2.2.4. Antioxidant activity**

146 The antioxidant capacity of our samples was measured using a Cary 5000 UV-visible spectrometer from  
147 Agilent Technologies and a solution of 2,2-diphenyl-1-picrylhydrazyl (DPPH) and ethanol. The antioxidant  
148 capacity was determined by averaging three measurements for each of the samples. The mean value was  
149 reported as the result and the standard deviation as the error bars. The films (5 mg) were dipped into the

150 DPPH and ethanol solution (25 mg of DPPH in 100 ml of ethanol) and then shaken and let to rest in dark  
151 conditions for 15 minutes at 23°C with a humidity of 50%. The absorbance was collected at the maximum  
152 absorption (517 nm) at room temperature at different times. A decrease in the absorbance of the DPPH  
153 solution indicates an increase of the antioxidant activity, which is qualitatively estimated by comparing  
154 their capacities to trap the DPPH:

$$155 \quad \% \text{ of DPPH inhibition} = (A_b - A_s / A_b) \times 100$$

156 with  $A_b$  being the Blanc (DPPH + EtOH) absorption and  $A_s$  being the sample absorption.

157

### 158 **2.2.5. Food packaging evaluation**

159 **Food simulation.** A simulation in contact with banana was performed to determine if an application of  
160 food packaging was possible. Packaging was prepared from aluminum sheets (hermetic to oxygen) with a  
161 hole in it, where our samples were placed so that it allows an exchange with the outside. Thus different  
162 packaging was prepared from the TOCN, TOCN/PVA and TOCN/PVA-PPy films. The TOCN/PVA-PPy  
163 film was dipped in an HCl solution (0.5 M) for 48 hours to eliminate the leaching before being used. Pieces  
164 of bananas were placed in contact with the films and let stand for 5 days at room temperature before  
165 opening the package. The control was kept in open air at room temperature for 5 days.

166 A second test was performed in noncontact with a piece of banana. The banana was placed in small flasks  
167 that were hermetically closed (sealed) with our samples (TOCN, TOCN/PVA and TOCN/PVA-PPy) with  
168 an exchange surface of 7 cm<sup>2</sup> for 5 days.

169 **Organic and inorganic leaching.** The iron measurements were performed using the PerkinElmer Optima  
170 4300 DV ICP-OES instrument. A Total Organic Carbon Analyzer (TOC-VCPH, Shimadzu Corporation)  
171 was used to analyze the TOC content in the filtrate and the results are given in ppm. The absorbance of a  
172 rising solution was measured in the UV-visible spectra with a Cary 5000 UV-visible spectrometer from  
173 Agilent Technologies. The concentration of pyrrole was determined by Beer's Law with an absorbance at  
174 290 nm. The pyrrole extinction coefficient used was determined experimentally at 67.7 L/mol/cm.

### 175 **2.2.6. Soil biodegradability evaluation**

176 The degradation tests for the TOCN and TOCN/PVA/PPy films was carried out in aerobic soil conditions  
177 with natural microorganisms. The samples did not undergo preliminary treatment before being buried in the  
178 soil (pH = 6.0). The test was led in relative humidity of 50–60%, which was maintained by spraying water,  
179 and the temperature was set to 22–24°C. The buried nanocomposites were controlled for 4 months. The  
180 films decomposition by soil microorganisms was evaluated by measuring the weight loss, during this  
181 period, using a digital balance with a precision of ± 0.001 g. The Soil pH was also evaluated after each  
182 measurement of degradation to determine the impact of the samples on the soil.

183

## 184 **3. RESULTS AND DISCUSSION**

### 185 **3.1. Morphology and structure of the composite**

186 Figure 1 shows the ATR-FTIR spectra of TOCN (a), TOCN/PVA (b) and TOCN/PVA-PPy (c) films. The  
187 absorbance of the –OH bonds, measuring approximately 3330 and 1340 cm<sup>-1</sup> for the TOCN, appears on  
188 each of the three spectra. The band at 1380–1310 cm<sup>-1</sup> is attributed to the anti-symmetric COO<sup>-</sup> stretching  
189 or aliphatic C–H deformation (Araki, Wada & Kuga, 2001). The peaks at 2895 cm<sup>-1</sup> correspond to the C–H and  
190 C–C bond, the peak at 1600 cm<sup>-1</sup> corresponds to the C–O function and finally the peak at 1024 cm<sup>-1</sup>  
191 corresponds to the C–O–C bonds. Additionally, the spectrum of TOCN/PVA-PPy shows a small peak at  
192 1734 cm<sup>-1</sup> that is attributed to the C=C stretching of polypyrrole (Aguilar-Hernandez & Potje-Kamloth, 1999). The  
193 strong peaks near 1070 and 760 cm<sup>-1</sup> present the doping state of polypyrrole and the N–H wagging, whereas  
194 the peak at 1030 cm<sup>-1</sup> is attributed to N–H stretching vibrations, and the peak at 1240 cm<sup>-1</sup> results from the  
195 interaction between the N–H bending vibrations and the C–N stretching (Clothup, Daly & Wiberley, 1990).

196 Moreover, the band at  $1330\text{-}1310\text{ cm}^{-1}$  demonstrates the C–H and C–N in-plane deformation vibration. All  
197 of the results demonstrate nearly the same peak positions of the main IR bands, which are associated with  
198 the structure of the PPy.

199

200 *Figure 1: ATR-FT-IR spectra of TOCN (a), TOCN/PVA (b) and TOCN/PVA-PPy (c) films.*

201 The SEM images show a cross section of the TOCN (Figure 2a). The TOCN structure is arranged in  
202 sheets/layers and it presents a dense arrangement of fibers. Nano and microfibrils create a huge  
203 entanglement network in bilayers, as is visible in Figure 2a. It is possible to see that on the upper face, the  
204 fibers have sedimented in a structure of a few  $\mu\text{m}$  in thickness, whereas the underside is flat and chains are  
205 clearly organized in multiples sheet layers. This could be explained by the fiber length distribution as the  
206 TOCN gel is composed of various lengths ranging from nano- to microscale. Thus, smaller fibers will  
207 sediment at a much slower rate and will be found in increasing concentrations in the upper section of the  
208 film. Unlike the underside, the dense upper portion has a variable thickness of a few micrometers. The  
209 PVA, which is not really visible on the SEM images, allows for improved mechanical properties and  
210 composite flexibility.

211 The chemical polymerization of pyrrole gives a layer of PPy nanoparticles on the surface of the TOCN/PVA  
212 film. The cellulose structure disappears under the conjugated polymer, which completely covers the film.  
213 The cauliflower structures of PPy are visible in Figure 2c (Shinde, Gund, Dubal, Jambure, & Lokhande, 2014).  
214 The polymerization-induced adsorption process does not allow for a completely uniform layer on the surface  
215 of the oxidized cellulose film. The agglomeration of conjugated polymer was not controlled, and the polymer  
216 chains are prone to deposit as irregular nanoparticles or aggregates as visible in Figure 2c (few micrometer  
217 aggregates). As shown in Figures 2a and 2b, a cross section of the TOCN/PVA-PPy shows that it is thicker  
218 than the TOCN/PVA film because of the PPy layer to the film surface. In fact, the average thickness of the  
219 composite was determined to be  $41\ \mu\text{m} \pm 2.3\ \mu\text{m}$  against  $34.2\ \mu\text{m} \pm 2.2\ \mu\text{m}$  (Table 1). The layer of PPy was  
220 estimated at  $7\ \mu\text{m}$ . Due to the arrangement of the PPy particles on the surface, the thickness of the dense part  
221 of the sample is more important. In the middle, the composite presents the same structure as the TOCN/PVA  
222 film with the other two parts (sheet and dense structure). Thus, the polymerization of pyrrole was performed  
223 on all the surfaces of our composite supported by the reinforcement of cellulose.

224 *Figure 2: SEM cross sectional micrograph of TOCN/PVA (a), TOCN/PVA-PPy (b) and the surface of TOCN/PVA-PPy*  
225 *film (c).*

226 A thin layer of PPy that is deposited on the substrate and affects the surface morphology of the film is  
227 analyzed by AFM. Figures 3a and 3b show the topography of the TOCN and TOCN/PVA-PPy and the  
228 roughness values are listed in Table 2. The roughness of the TOCN films is more important than the two  
229 other films whereas we note that the addition of PVA fills the pores generated by cellulose fibers, leading  
230 to a more planar roughness. The structure of the TOCN films is clearly homogeneous, as seen in Figure 3c.  
231 The PPy layer leads to a cauliflower structure and slightly increases the roughness of the composite,  
232 compared to the TOCN/PVA film. The surface heterogeneity and roughness increase because we did not  
233 completely control the chemical polymerization that leads to the formation of some of the PPy aggregates.  
234 For this reason, it is difficult to obtain clear AFM images of the TOCN/PVA-PPy film as increased  
235 roughness interfere with the actual capability of the AFM to measure efficiently (Figure 3d).  
236

237 *Figure 3: Surface topography of the TOCN (a), TOCN/PVA-PPy (b), and AFM topographical images of TOCN (c),*  
238 *TOCN/PVA-PPy (d).*

239 **3.2. Determination of the barrier properties of TOCN/PVA-PPy**

240 **Air permeability.** One of the main purposes of food packaging is the high barrier properties to limit the  
241 interaction with the outside. Table 2 shows the air permeability, oxygen transmission rates and the water  
242 vapor transmission rate of the fabricated films.

243 *Table 2: Barrier properties and roughness of the TOCN, TOCN/PVA and TOCN/PVA-PPy films.*

244 TOCN is known to be a strong gas barrier material, so it is natural to see that the structure of our TOCN  
245 films are very tight ( $7.2 \times 10^{-3} \text{ cm}^3/\text{m}^2 \cdot \text{Pa} \cdot \text{s}$ ) and our samples have similar structures. As a result, the ability  
246 of air to pass through the samples is relatively small. This can be explained by the morphology of our films.  
247 As seen in the cross-sectional SEM, the film is in two parts with one part being very dense. The dense part  
248 is sufficiently full to limit the passage of air through the film. The differences obtained between our  
249 samples are not significant enough to be meaningful, which is why we compared the results to those of a  
250 reference sheet of paper to assess the capabilities of our samples. It is also possible to see that our samples  
251 show very good barrier properties ( $\times 100$ ) to air compared to the sheet of paper. These properties are  
252 therefore due, in part, to the cellulose making up the structure of the films. The presence of the polypyrrole  
253 nanoparticles on the surface, does not improve these properties. As it is required for food packaging, it is  
254 coherent that low air permeability is already achieved.

255 **Oxygen Permeability.** Oxygen has been known to play an important role in the degradation of foodstuffs. It  
256 is necessary to use materials with good oxygen barrier properties to extend the life of food (Bradley, Castle &  
257 Chaudhry, 2011). Oxygen permeability is therefore an important parameter for food packaging materials. The  
258 oxygen transmission rates of TOCN films with a thickness of  $31 \mu\text{m}$  were as low as  $83.8 \pm 0.6 \text{ cm}^3/\text{m}^2 \cdot \text{day}$ ,  
259 at an 85% RH after 400 min. Recently, Aulin (Aulin, 2009) and Osterberg et al. (Osterberg et al., 2013)  
260 demonstrated that oxygen permeability of TOCN films increases with the increase in relative humidity  
261 because of the swelling of nanofibrils through the adsorption of water molecules at a high relative humidity.  
262 According to these studies, it can be assumed that by lowering the relative humidity, the OTR becomes  
263 relatively low. Thus, the TOCN films also present tunable barrier properties. The OTR values of the  
264 TOCN/PVA-PPy ( $16.5 \text{ cm}^3/\text{m}^2 \cdot \text{day}$ ) and TOCN/PVA ( $71.8 \text{ cm}^3/\text{m}^2 \cdot \text{day}$ ) films were lower than those of the  
265 TOCN films. The incorporation of PVA chains allows the reinforcement of the dense network formed by the  
266 nanosized fibrils by increasing the hydrogen bonding potential. This explains the decrease in the OTR values  
267 of the TOCN/PVA, compared to the pure TOCN. The reason for the greater decrease in the OTR values  
268 (down 80%) of the TOCN/PVA-PPy is due to the polypyrrole particles, which fill the pores of the film, thus,  
269 making the structure of the composites even more compact. The compact structure of the composites shown  
270 in the SEM images can explain such high barrier properties. The values of the TOCN/PVA-PPy are  
271 competitive with synthetic polymers used in food packaging, such as polyvinyl alcohol ( $14 \text{ cm}^3/\text{m}^2 \cdot \text{day}$ ) or  
272 polyethylene terephthalate ( $19 \text{ cm}^3/\text{m}^2 \cdot \text{day}$  and a film thicknesses of  $12 \mu\text{m}$ ) (Johansson & Clegg, 2014).

273 **Water vapor permeability.** Even if the gas barrier properties of the TOCN films are competitive with  
274 synthetic polymers, their water vapor transfer rate remains very high and remain non-competitive. The  
275 water vapor transmission rates of our samples are shown in Table 2. The TOCN films exhibit slightly  
276 higher values ( $276 \text{ g}/\text{m}^2 \cdot \text{day}$ ) than what can be found in the literature ( $234 \text{ g}/\text{m}^2 \cdot \text{day}$ ). These values are  
277 mainly due to the strong hydrophilic nature of the cellulose nanofibers. Moreover, we can attribute this  
278 decrease in the barrier properties to the decreasing hydrophobicity as evidenced by the increase in the water  
279 contact angle (Nair et al., 2014). However, the hydrophilic nature of the films is not the only criteria to have  
280 low-water vapor barrier properties. The structure also plays an important role, since the water will have  
281 difficulty in diffusing through if the structure is very dense.

282 The addition of the PVA chains increases the dense network, which explains a slight increase in the water  
283 vapor barrier properties ( $207 \text{ g}/\text{m}^2 \cdot \text{day}$ ). The film structure is compact; therefore, less water can penetrate  
284 and it limits the water vapor transfer rate. The TOCN/PVA-PPy showed an important enhancement in the

285 water vapor barrier property at 50% relative humidity (18 g/m<sup>2</sup>.day). The PPy layer at the surface of the  
286 film plays the role of protection against water permeation. The PPy is known for its hydrophobic character  
287 and the layer protects the TOCN/PVA film. The nanoparticles deposited on the surface (Figure 2c) also  
288 help to fill the pores of the films. This result is competitive with current commercial films made from  
289 synthetic polymers, such as polyethylene (16.8 g/m<sup>2</sup>.day) (Jester, 2005). The barrier efficiency of this  
290 composite is highly competitive and comparable with commercial synthetic polymers. To confirm, Figure 4  
291 shows the oxygen permeability and water vapor transmission rate of our films compared with those from  
292 commercially available synthetic polymers and biopolymers. Thus, this composite opens vast possibilities  
293 for food packaging applications utilizing cellulose-based materials.

294 *Figure 4: Oxygen permeability= f (Water Vapor Transmission Rates) – Polymer films compared to TOCN, TOCN/PVA*  
295 *and TOCN/PVA-PPy films. Green points: Biopolymers; Dark points: petroleum polymers. Adapted from Jester (2005).*

### 296 **3.3. Antioxidant activity**

297 Several studies have examined the antioxidant activity of polypyrrole (reduced DPPH) (Zare, Lakouraj &  
298 Mohseni, 2014; Gizdavic-Nikolaidis, 2004). This property depends on the capability of the PPy to donate active  
299 hydrogen atoms or transfer electrons to reduce the DPPH. However, the preparation method, size, material  
300 or chemical structure of the PPy play major roles in its antioxidant activity to reduce DPPH. Moreover, it is  
301 known that the antioxidant effects allow extending the life of food with this type of packaging properties,  
302 which are the subject of extensive research. To evaluate the antioxidant character of TOCN/PVA-PPy  
303 filmz, we have decided to evaluate the scavenging activity of DPPH as a stable free radical. We placed our  
304 samples in a DPPH solution at different times (15 min, 1 and 120 hours). The absorbance of DPPH  
305 decreases with antioxidant activity (percent of inhibition increase) and the percent of DPPH inhibition is  
306 reported in Figure 5.

307 *Figure 5: Antioxidant property assessment of TOCN, TOCN/PVA and TOCN/PVA-PPy films.*

308 Each sample thus demonstrated a DPPH inhibition capacity. Nevertheless, it is possible that after 5 days,  
309 the DPPH sample is slightly degraded and could also explain a significant inhibition from the TOCN and  
310 TOCN/PVA films. However, to demonstrate superior inhibition capabilities (3x) of the TOCN/PVA-PPy  
311 with respect to the TOCN/PVA film. We can see an increase in the rate of inhibition of the DPPH with  
312 time. After only 15 minutes, the PPy exhibits a high reducing (28%) and interacts quickly with the DPPH,  
313 while the TOCN/PVA film shows only a very low activity. As demonstrated in previous work (Gizdavic-  
314 Nikolaidis, 2004), polypyrrole based composites have a strong antioxidant property, conferred by chains of  
315 PPy owing to its redox active nature that reduces this radical. This important activity is clearly visible after  
316 one hour, when the DPPH inhibition reaches 63%, three times more than the TOCN/PVA film. After five  
317 days, the antioxidant properties tend to a maximum inhibition (68.8%) allowed by the chains of  
318 polypyrrole. A small portion of the PPy, which is less accessible, explains the slight increase until the  
319 maximum.

### 320 **Food simulation for active food packaging applications**

321 **Food simulation by contact.** To evaluate the possible leaching of molecules contained in the  
322 *TOCN/PVA-PPy* composite, we have realized several rinsing steps of our composite using different  
323 solvents (water or HCl solution) and different processes (dipping for 48 hours or Accelerated Solvent  
324 Extraction (ASE)). Rinses of the solutions were then analyzed by ICP, TOC and UV-visible. The results are  
325 shown in the Table 3.

326 *Table 3: Concentration of iron, carbon and pyrrole in supernatant after rinsing the TOCN/PVA-PPy composite with*  
327 *different solvents.*

328 The results show that the HCl dipping allows eliminating more iron ions (49.7 mg/L) than water (0.5 mg/L)  
329 for the same process (dipping). Accelerated Solvent Extraction is a more aggressive technique with a high  
330 pressure and temperature (120°C). It allows eliminating 20.8 mg/L, in only 20 minutes, and 1900 ppm of  
331 carbon against 65 with HCl solution. No black particles were visible in the supernatant, so we assume that  
332 the carbon concentration is from the cellulose chains or unpolymerized pyrrole molecules. Analysis was  
333 performed using the UV-visible spectrometer to determine the concentrations of pyrrole present in the  
334 supernatant. The concentrations are relatively low for each one; however, the ASE, which is more  
335 aggressive, eliminates more traces of the pyrrole. Therefore, all of the tests of food simulation by contact  
336 were carried out after dipping in the HCl solution and the results are shown in Figure 6. The TOCN/PVA-  
337 PPy film attests to an improved conservation of bananas after five days compared to the control or the film  
338 TOCN. With the control (five days in ambient air), banana browned and was dehydrated before showing  
339 rot, as evidenced in Figure 6. In the presence of the cellulose film, bananas remained hydrated, but began to  
340 deteriorate (Figure 6b), as we can see with the brown color of the banana from the oxidation of this one by  
341 oxygen. This oxidation is also responsible for the degradation of the banana. As seen in Figure 6c, the  
342 banana pieces are retained after five days. This result shows the notable barrier properties of the composite.

343 *Figure 6: Schema of food packaging test by contact (a); food simulation after 5 days, with the TOCN film (b),*  
344 *TOCN/PVA-PPy (c); schema of food packaging test by noncontact (d); food simulation flasks (left: TOCN/PVA-PPy*  
345 *and right: TOCN/PVA films) (e); piece of banana after 5 days (f).*

346 **Noncontact food simulation.** To limit carbon and iron transfer from the composite to the food, we have  
347 considered a noncontact packaging method. The flasks were sealed so that the only possible exchanges with  
348 the outside are made through the film (figure 6e). In Figure 6f, we can see that banana is better preserved  
349 with the TOCN/PVA-PPy than the TOCN or the TOCN/PVA films. No brown color is visible, so there is  
350 no trace of oxidation, unlike the other two trials. This test demonstrates the good barrier property against  
351 oxygen, which due to the presence of the PPy particles.

### 352 3.4. Soil biodegradability

353 Figure 7 shows the evolution of the soil pH and the in vitro degradability of the TOCN and TOCN/PVA-  
354 PPy films, which were evaluated under soil burial condition. The TOCN film decomposed more quickly  
355 than the TOCN/PVA-PPy (-20% against -10%). However, the degradation curves follow the same  
356 degradation rate trend over time. The degradation of the TOCN/PVA-PPy, which is lower than the  
357 cellulose film, is explained by the presence of polypyrrole, which requires more time to degrade. Vegetable  
358 cellulose fibers are the first to deteriorate, which is why we observe the same trend for both curves. After  
359 100 days of being buried, the films exhibited degradation rates of 38% and 53%, respectively. The  
360 degradation phenomenon is not without effect on the soil due to the release of constituents of different  
361 films. For this reason, we assessed the impact of the breakdown of films on the soil pH. With degradation,  
362 the pH increases continuously up to 7.2, an increase of one unit. The soil pH is neutral, so it is difficult to  
363 deduce the real impact of this degradation.

364 *Figure 7: Decomposition of films in the soil (solid line for TOCN/PVA-PPy; solid double line for TOCN) and evolution*  
365 *of the soil pH (dash dot line for TOCN/PVA-PPy; double dash dot line for TOCN).*

## 366 367 4. CONCLUSIONS

368 We report the synthesis of a TOCN/PVA-PPy film by chemical polymerization of pyrrole at the surface of  
369 TOCN. Nanocellulose has opened vast possibilities of utilizing cellulose-based materials to be substitutes  
370 for plastics. The use of TOCNs in composite films with a coating was found to substantially reduce the  
371 oxygen permeability of the material. The oxygen barrier and water vapor permeability efficiency of the



372 TOCN/PVA-PPy films are highly competitive and even comparable with commercially available synthetic  
373 polymers. The improvement in the barrier properties and antioxidant activity can be attributed to the  
374 polypyrrole particles which coat the dense network formed by nanofibrils. In addition, we have  
375 demonstrated two different applications of food packaging for this composite. The combination of barriers  
376 and antioxidant properties allows the TOCN/PVA-PPy films to improve the shelf life of perishable foods  
377 and protect the food from dirt, dust or oxygen. The dark color of the films may also protect food from light  
378 degradation. The biodegradable character could also reduce packaging waste generated by plastics.

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