Natural additives to enhance the barrier properties of nanocellulose films

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ABSTRACT

Finding alternatives to fossil-based materials is one of the most important challenges of our time. Since cellulose is the most abundant natural polymer on the planet, its use to solve this challenge would be ideal. In the present work, cellulose nanocrystals (CNC) were mixed with different plasticizers to obtain films with improved properties. To this aim, a first study was conducted in order to find the optimal amounts of plasticizer which maximize the compatibility with nanocellulose. The studied additives were Sorbitol (Sor), Glycerol (Gly), Maltitol (Mal), Xylitol (Xyl), Mannitol (Man), Gellan gum (Gg), and Ethylene glycol (Eg). The addition of these plasticizers to the CNC matrix was expected to improve the film flexibility and workability, which is one of the major limitations of this polymer. The selected plasticizers show similar structure to nanocellulose, with free hydroxyl groups which allow compatibility with nanocellulose, resulting in homogeneous films. The films with different amounts of additives were characterized in terms of barrier properties, crystallinity, SFE (surface free energy), and biodegradability. The barrier properties of the films were analyzed in terms of air, oil, water, water vapor and oxygen permeabilities. Results show that all additives decreased air and water permeance, to a greater or lesser extent. CNC films with Mal, Sor, and Xyl had a better oxygen barrier than the control, showing a total oxygen resistance at RH below 60%. About WVTR at moderate (50%) and drastic (90%) humidity, Mal and Gg showed values below the control. Films containing Mal provided the best barrier properties to oxygen and water vapor transmission. The interaction of the films with other compounds (liquids or adhesives) was observed through SFE. In relation to biodegradability, all the additives increased the biodegradability of CNC-based films when subjected to a biodegradability test under controlled composting conditions. These biodegradability results are relevant in terms of the environmental impact of the films, especially if the films are intended to provide a sustainable alternative to traditional food packaging materials.

Keywords: *cellulose nanocrystals, additives, barrier properties and biodegradability*

INTRODUCTION

Traditionally, petroleum-based plastics have been the materials used for food packaging, which has led to serious health and environmental problems [1]. Finding alternatives to fossil-based materials is one of the most important challenges of our time. Since cellulose is the most abundant natural polymer on the planet, its use to solve this challenge would be ideal. We need to find a material that meets the requirements of acting as a barrier to different agents, but is also environmentally friendly. Nanocellulose is a very interesting material for the food packaging industry, as it meets environmental requirements and also has certain barrier properties [2]. However, the problem is the presence of moisture [3]. The process of obtaining CNC involves hydrolysis of the amorphous part, usually with sulphuric acid, giving rise to

crystalline cellulose nanostructures [4,5]. CNCs possess a large number of surface hydroxyl groups, and a high surface area because of the dimensional structure of CNCs, allowing a strong interaction with other matrices to form nanocomposites [6]. CNC films are highly rigid and brittle and hence difficult to handle. These shortcomings have been addressed by previously mixing CNCs with a plasticizer. The surface of CNCs contains easily accessible hydroxyl groups that may interact with those in plasticizers, thereby altering the morphology of the crystals and conferring them new properties [7]. In this study, we compared the effects of various additives on the properties of CNC films with a view to identifying the appropriate amount and type of plasticizer that is more compatible with nanocellulose. To achieve good compatibility with nanocellulose, seven additives, namely, sorbitol (Sor), glycerol (Gly), maltitol (Mal), xylitol (Xyl), mannitol (Man), gellan gum (Gg), and ethylene glycol (Eg), were selected and tested in CNC-based films. These plasticizers have a structure similar to nanocellulose, with free hydroxyl groups, making them more compatible to join with nanocellulose and form a homogeneous film. The resulting films with different amounts of additives were characterized in terms of barrier properties, crystallinity, and biodegradability.

EXPERIMENTAL

A 3% suspension of CNC were deposited on a polystyrene plastic plate and allowed to evaporate under controlled humidity (50% relative humidity (RH)) and temperature (23 °C) conditions, for about 5 days. To overcome the brittle nature of CNC films, plasticizers such as Sor, Gly, Mal, Xyl, Man, Gg, and Eg were used and applied in different percentages (10, 15, 20, and 25%) of the dry weight of CNCs. Air permeability was measured following the standard ISO 5636-3:2013, by the Bendtsen method. Water absorption (water drop test (WDT)) was evaluated using the TAPPI T835. The hydrophobicity was measured by the water contact angle (WCA). WCA measurements were performed using a Dataphysics OCA15EC contact angle goniophotometer. Oil resistance was measured in accordance with the standard ISO 16532-3:2010 (turpentine test). Oxygen permeability (OP) was measured using MOCON OX-TRAN Model 1/50 with an atmospheric oxygen concentration of 100% at 23 °C temperature and at different RHs (20, 40, 60, and 80%). The water vapor transmission rate (WVTR) was measured according to the standard procedure ISO 2528 (2017) at 25 °C and at two RHs, 50 and 90% RH. The surface free energy SFE was evaluated using the Owens, Wendt, Rabel, and Kalble (OWRK) method [8]. CNC films were subjected to X-ray diffractometry analysis. The crystallinity index (CI) was calculated based on Segal et al., 1959 method [9].To study the final aerobic biodegradability of the films the methodology of the UNE-EN ISO 17556 standard was adapted.

RESULTS AND DISCUSSION

Barrier properties. All additives decreased air permeance to values from 0.95 ± 0.10 to 1.69 ± 0.07 μm Pa^{-1} s^{-1}; however, the dose of plasticizers did not influence this property. The lowest permeance was that of the film containing 10% Sor and the highest that of the Gg-containing films (Table 1). We measured oil resistance in the films containing a 10 and 25% dose of each additive and in the control film for comparison. All CNC samples showed no penetration of oil through the films (relative rate of oil penetration higher than 1800 s); therefore, they were oil proof. Table 1 shows the time needed by each film to absorb a drop of water as measured with the WDT. The additives further decreased the water absorption capacity of the films, and this

effect was more pronounced when the additive dose was increased. All additives except for Gg caused a slight decrease in WCA (table 1).

Table 1. Air permeability (μm Pa^{-1} s^{-1}), WDT (min) and WCA (º) of the CNC-control film and CNC based film additives (10 and 25%).

	CNC	Sor		Gly		Mal		Xyl		Man		Gg		Eg	
(%)		10	25	10	25	10	25	10	25	10	25	10	25	10	25
Air per m.(μm Pa^{-1} s^{-1})	2.48 ± 0.14	0.95± 0.10	1.57± 0.04	1.49± 0.09	1.55 ± 0.10	1.38 ± 0.09	1.45 ± 0.08	1.49 ± 0.03	1.44 ± 0.05	1.49± 0.09	1.25 ± 0.06	1.69 ± 0.07	1.73± 0.15	1.58 ± 0.11	1.61 ± 0.06
WDT (min)	53.19± 5.50	70.2± 0.39	78.22 ± 3.87	60.65 ± 3.23	74.4 ± 0.86	70.42± 2.19	73.24± 5.64	62.19± 2.33	73.92± 3.19	68± 1.95	71.7 ± 6.74	62.3 ± 2.14	65.8± 3.18	59.5 ± 2.86	64.8 ± 4.92
WCA (º)	53.2 ±0.09	46.82 ±3.87	48.72 ±3.96	46.22 ±0.24	51.7 ±1.66	50.5 ±7.8	44.6 ±2.35	43.6 ±7.15	45.4 ±7.15	45.47 ±3.18	49.2 ±5.19	74.5 ±6.56	90.45 ±5.68	44.1 ±5.87	47.4 ±3.91

The WVTR was measured at 50 and 90% RH in those films that contained 25% of additives (Fig 1), and all of them (except Gly and Eg) reached lower WVTR values at 50% RH than the unplasticized film. The lowest WVTR was recorded for films that contained Mal. Only Mal and Gg were below the control at 90% HR.

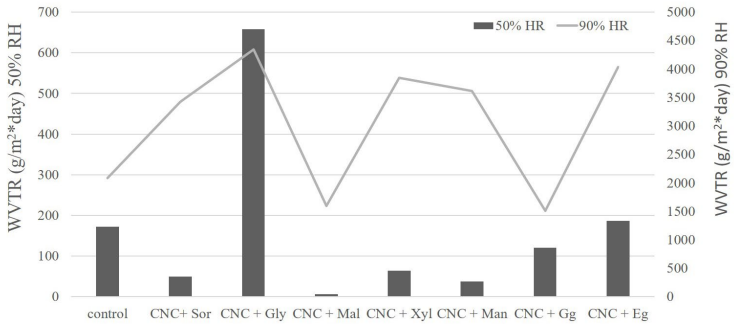

Fig 1. WVTR at 50% RH and 90% RH of the CNC-control film and CNC based film additives.

About OP, at 20% RH, the control film presented OP values of 1806 cm3·μm/m2·day·atm, being even higher at 40% RH. With the exception of Gly, additives provided films with better barrier properties compared to CNC control films. Interestingly, CNC-Xyl, CNC-Sor, and CNC-Mal films showed a total resistance to oxygen from 20% RH until 60% RH. From then on, the OP started to increase but always remained at values below the control at 40% RH.
Surface Free Energy (SFE). Values of SFE go from 34.32 to 48.47 mJ/m^2. The CNC films containing additives show different energy states depending on the additive. Sor, Gly, and Xyl films showed an increased polar component, indicating their polar nature. The polar and dispersive components of the films containing Mal, Eg, and Man were quite balanced. Finally, the film containing Gg was mainly dispersive, presenting also the lowest polar component.
Crystallinity index. The CI of the films was calculated from Segal et al. method [9]. The results show that crystallinity was slightly higher in the films containing 25% Sor (CI = 88.84%) or 25% Xyl (CI = 88.85%) than in the control film (CI = 88.75%). In contrast, crystallinity in the films containing 25% Man or 25% Gg was slightly lower than in the control film (85.66 and

82.1%, respectively). **Biodegradability.** After 90 days in compost, higher levels of degradation were found for the films which contained additives. The film that was more easily biodegraded was the one that contained Xyl followed by Gg, Sor, Gly, Mal, and Man. The evolution of biodegradability tested showed that the control film gives rise to a lower amount of accumulated CO_2, which suggested that the microorganisms have generated less CO_2 during their metabolism. The presence of these additives made them more accessible for the penetration of the enzymes produced by the microorganisms.

CONCLUSIONS

CNC-based films obtained by adding a plasticizer (Sor, Gly, Mal, Xyl, Man, Gg, or Eg) at different concentrations were characterized for barrier properties, their crystallinity and SFE in addition to their biodegradability. Based on the results, all additives decreased air and water permeance, to a greater or lesser extent. CNC films with Mal, Sor, and Xyl had a better oxygen barrier than the control, showing a total oxygen resistance at RH below 60%. The Mal and the Gg showed values of WVTR below the control (50 and 90% RH). Those containing Mal provided the best barrier properties to oxygen and water vapor transmission. The analysis of the SFE of the films revealed different behavior depending on the additive. All the additives increased the biodegradability of CNC-based films.

ACKNOWLEDGMENTS

This publication is part of the PID2020-114070RB-I00 (CELLECOPROD) project, funded by MCIN / AEI / 10.13039 / 501100011033.With the support of the Secretariat of Universities and Research of the Generalitat de Catalunya and the European Social Fund.

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