COST Action FP 1405

ActInPak (Active and intelligent fibre - based packaging)

HYDROPHOBIC LIGNOCELLULOSIC FILMS FOR PACKAGING APPLICATION

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1. INTRODUCTION

Bleached cellulose nanofibers (CNF) form films with excellent mechanical and barrier properties, especially against oxygen. However, cellulose is highly hydrophilic, which yields low water vapor barrier properties and poor compatibility with non-polar polymers. Additionally, surface modification of cellulosic nanofibers reduces their surface energy and polarity, potentially improving the adhesion of the fiber/matrix system in biocomposites. However, such modification is performed mainly in the hydroxyl groups of the glucose unit, decreasing the OH-bonding and its reinforcement performance.

On the other hand, lignin-containing nanofibers are stiffer and less hydrophilic than bleached CNF. Moreover, it has been demonstrated that lignin can facilitate the nanofibrillation of unbleached kraft pulp fibres thus improving the barrier properties of films due to an increase of the film density (Chinga-Carrasco et al., 2012). Besides, the presence of lignin in nanofibrillated non-bleached cellulose provides a new target for fiber functionalization.

Laccase is a multi-copper enzyme able to oxidize phenolic compounds, and it may promote the grafting of such compounds on lignin moieties. Hence, laccase could graft hydrophobic phenols onto unbleached cellulose nanofibers without decreasing the hydroxyl content of the cellulose. This enzymatic-mediated reduction of water wettability of nanofibrillated lignocellulose may lead to the production of reinforcement materials with remarkable mechanical and barrier properties, but also with proper compatibility with non-polar polymers.

In this work, films made of Kraft nanofibers (both bleached and unbleached) were enzymatically treated in the presence of a hydrophobic phenolic compound. Water contact angle and laser profilometry of the films were assessed. The enzymatic grafting is a promising environmentally-friendly strategy for the functionalization of lignin-containing nanofibers.

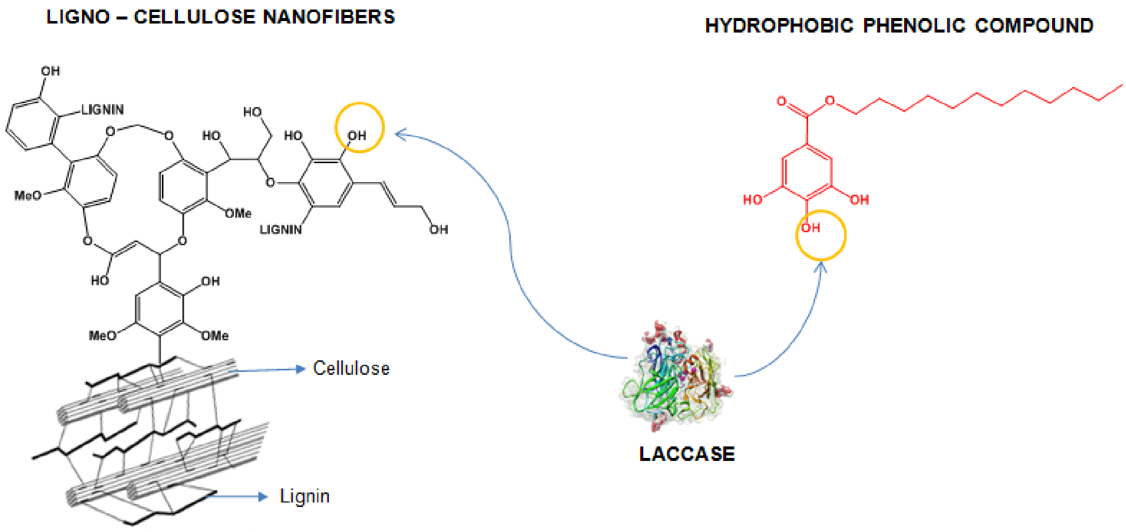

Fig. 1. Scheme of enzymatic hydrophobization of ligno-cellulosic nanofibers

2. PERFORMED ACTIVITIES

- **Enzymatic hydrophobization of films made from bleached-cellulose (B-NFC) and ligno-cellulose (L-NFC) nanofibers.** Films with a basis weight of 20 g / m^2 were prepared from B-NFC and L-NFC suspensions. After 5 days of drying process at room temperature (18-20 º C), each film was immersed in 34 mL of phosphate buffer solution (0.1 M, pH 7). In addition, 24 mL of acetone were added to assure the total solubility of the hydrophobic compound. The laccase dose was 235 U/film and the final concentration of lauryl gallate (LG) was 5 mM. The treatment was carried out at 50 ºC during 2 h. Each treated film was dried at 20 ºC during 24h and washed with 60 mL of water / acetone (50/50%, v/v) solution to remove the non-grafted hydrophobic molecules.

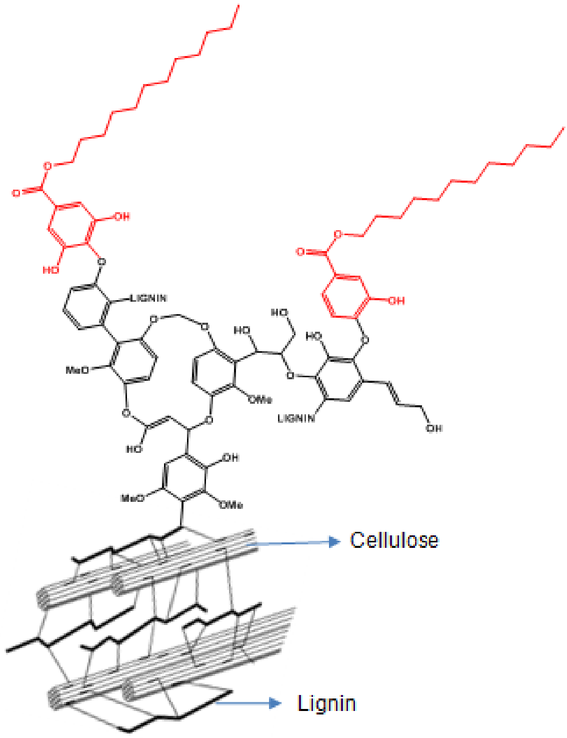

Fig. 2. Scheme of enzymatically hydrophobized ligno-cellulosic nanofiber

- **Water contact angle (WCA) measurement of the treated films.** The hydrophobicity of the enzymatically-treated films was evaluated by measuring the dynamic WCA.

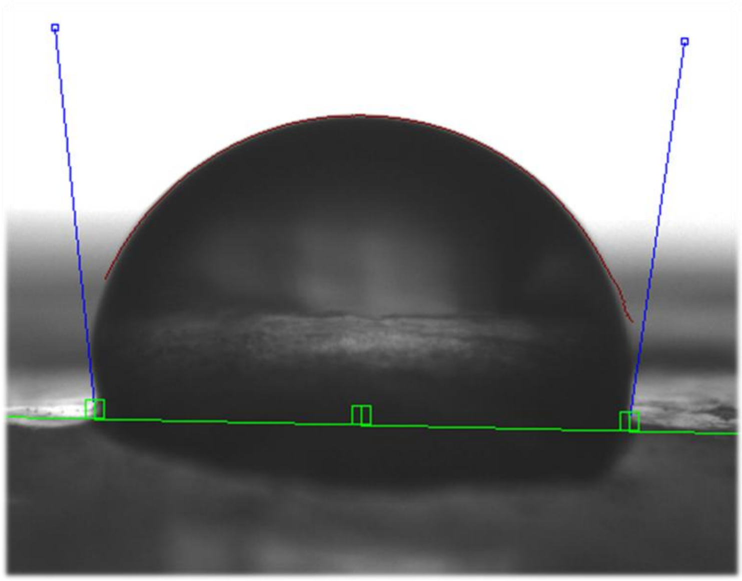

Fig. 3. Water contact angle measurement of a enzymatically-hydrophobized film made with ligno-cellulose nanofibers.

- **Films topography and morphology.** The surface profile and the roughness of the films was analyzed by laser profilometry (LP). Samples of 10 x 20 mm were coated with a layer of gold. 10 random images from the top side of the films and from each series were acquired. The resolution was 1 μm (micrometer) in the x,y direction and 10 nm in the z-direction. The roughness was quantified at various wavelengths as described by Chinga-Carrasco et al. (2014).

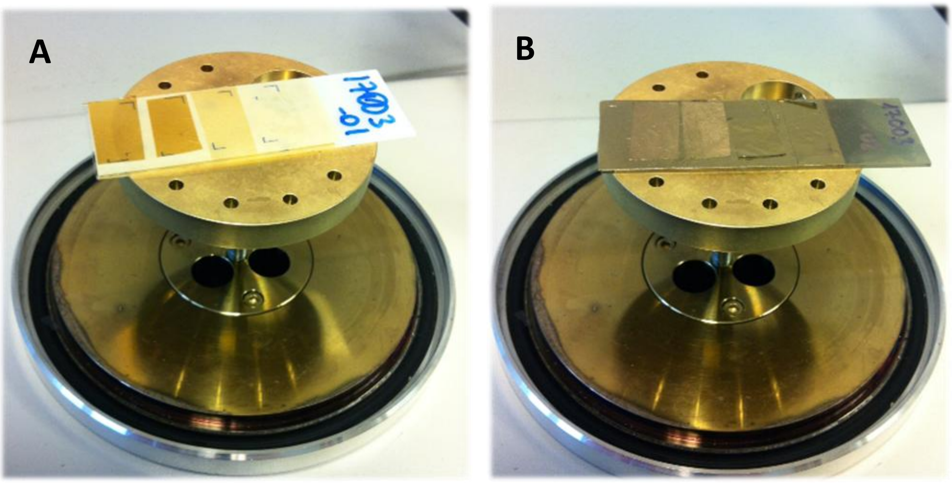

Fig. 4. Film samples (10 x 20 mm) before the coating with a layer of gold (A) and after the coating process (B).

- **Oxygen transmission rate (OTR).** The OTR was measured with a Mocon OX-TRAN® 1/50 test system (Mocon, Minneapolis, MN, USA) at 50% relative humidity and 23°C.

Fig. 5. Mocon OX-TRAN® 1/50 test system device

3. RESULTS

3.1. Water contact angle

Films made from bleached cellulose nanofibers (B-NFC) and lignin-containing cellulose nanofibers (L-NFC) were hydrophobized through laccase-assisted grafting of lauryl gallate (LG). Enzymatically treated films increased their water contact angle (WCA) after the enzymatic grafting of LG (Fig. 7). Enzymatically treated films made from unbleached nanofibers (L-NFC) yielded the highest hydrophobic properties. Such results were expected due to the grafting of LG onto the films surface. It is expected that the L-NFC nanofibers have lignin moieties on their surface structure, which facilitate the grafting of LG. Nevertheless, films made fully bleached cellulose nanofibers (B-NFC) showed remarkable hydrophobic properties after the enzymatic treatment. Theoretically, laccase enzyme should not be able to oxidize cellulose. Thus, the increase of WCA of the B-NFC films could be due to the diffusion of LG monomers within the film structure, which were polymerized during the enzymatic treatment. Such polymerization reaction probably created a network of LG which remained in the film structure even after the aggressive washing process (Fig. 6).

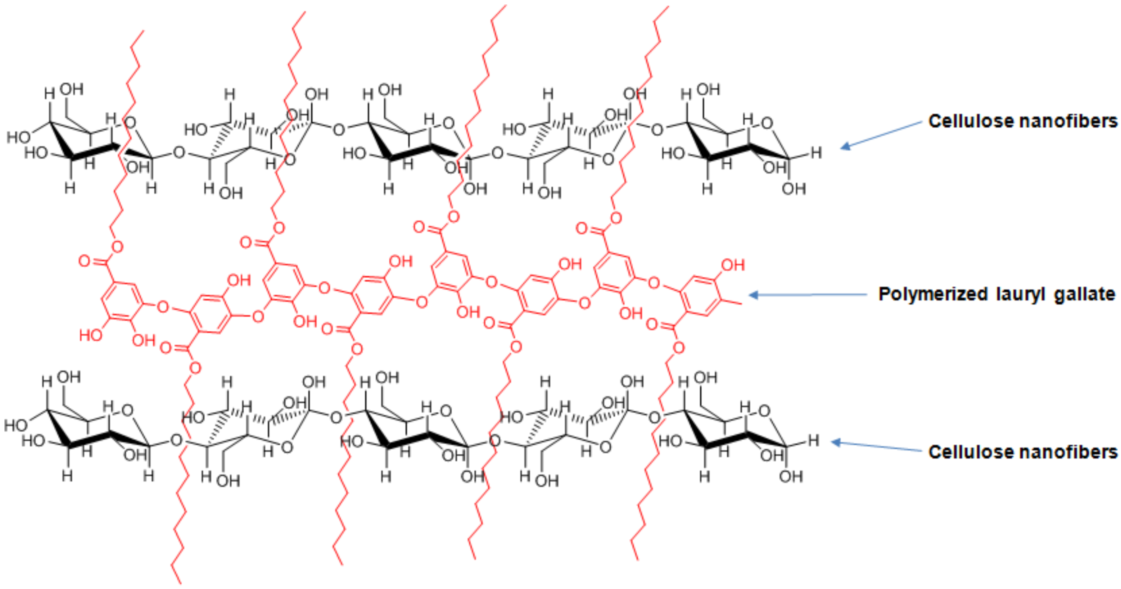

Fig. 6. Proposed mechanism of enzymatic hydrophobization of films made from bleached cellulose nanofibers.

Regarding the non-treated films, L-NFC films evidenced higher WCA than B-NFC films. Such results were expected since lignin provides hydrophobic properties to cellulose nanofibers.

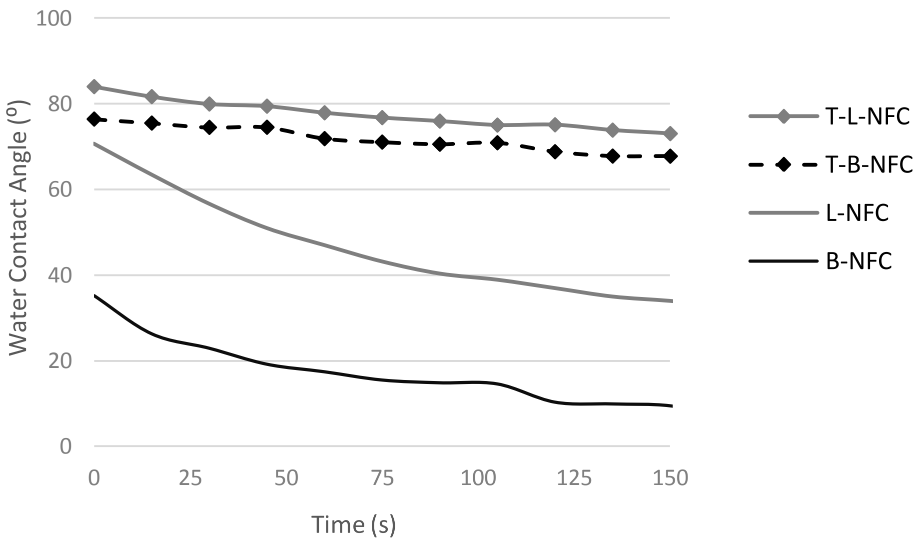

Fig. 7. Water contact angle of films made of: Bleached cellulose nanofibers (B-NFC); Ligno-cellulosic nanofibers (L-NFC); T: enzymatically grafting treatment.

3.2. Laser profilometry

The surface profile of the films was studied before and after the enzymatic grafting. The surface roughness (Sq) which was assessed at wavelengths lower than 160 µm showed that the enzymatic treatment affected the films surface morphology (Fig. 8).

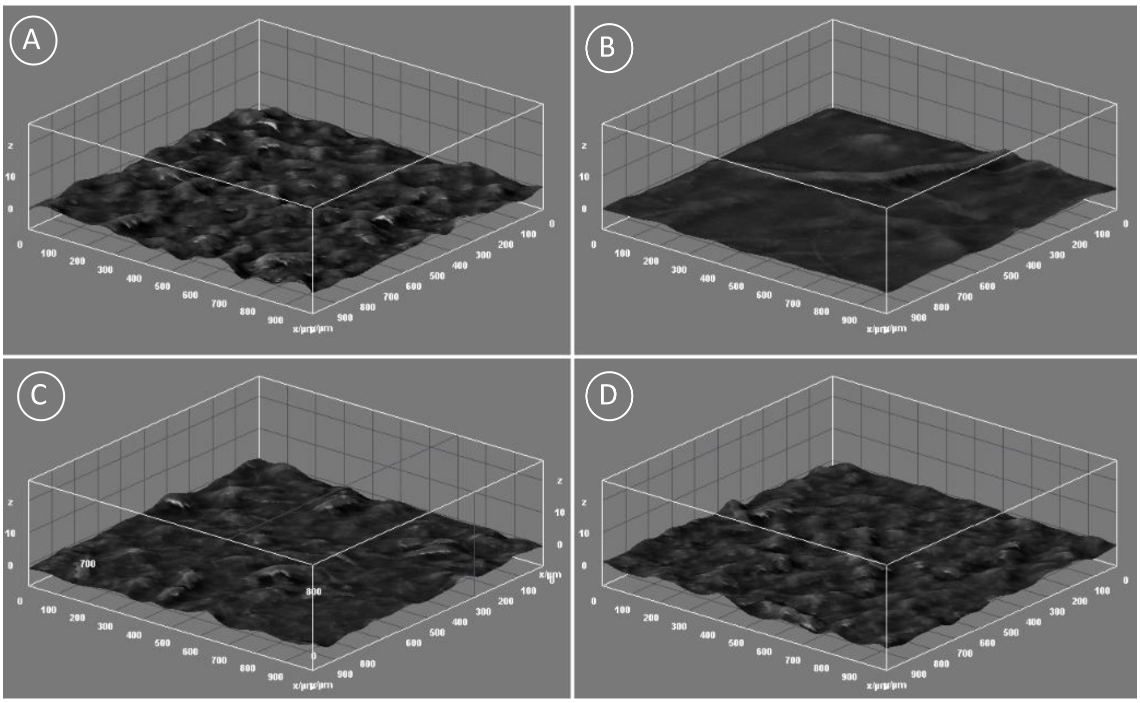

Fig. 8. Surface topography of the films made from: A) bleached cellulose nanofibers; B) bleached cellulose nanofibers treated enzymatically; C) ligno-cellulose nanofibers; D) ligno-cellulose nanofibers treated enzymatically.

The grafting of LG onto L-NFC films increased slightly the surface roughness. However, the enzymatic treatment of B-NFC films produced smoother surfaces than the non-treated films (Fig. 9). As it was shown in Fig. 5, it was not expected that LG graft onto the surface of the B-NFC films. Hence, the hard conditions of the washing process, with a 50 % of acetone at 50 ºC, probably contribute to soften the film surface.

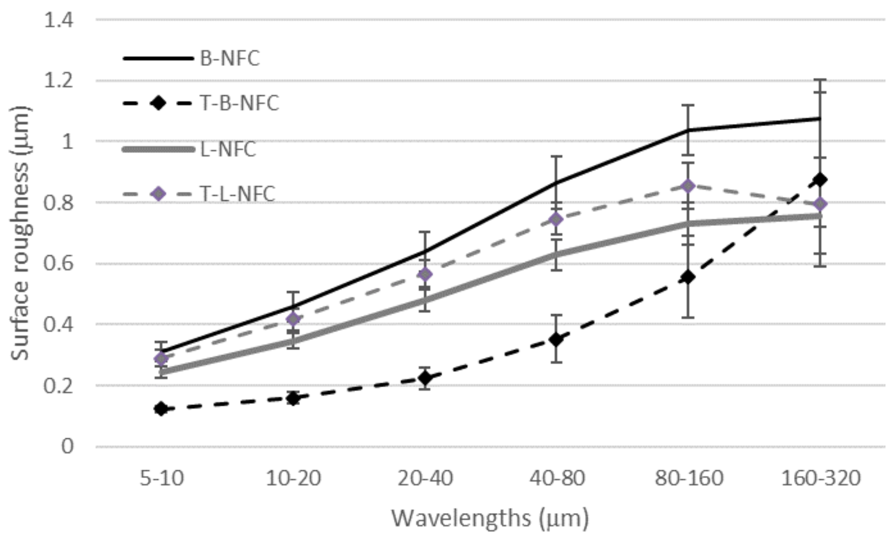

Fig. 9. Surface roughness at different wavelengths. Films made from bleached cellulose nanofibers (B-NFC) and unbleached cellulose nanofibers (L-NFC). T: treated enzymatically.

3.3. Oxygen transmission rate (OTR)

The OTR was assessed in order to know whether the enzymatic hydrophobization provides barrier properties to the films. However, it was not possible to measure the barrier properties of the treated films since the results obtained were out of the measuring range. Therefore, the values obtained were not reliable. The washing process after the enzymatic treatment could affect the barrier properties of the films.

4. CONCLUSIONS

Films made from bleached and lignin-containing cellulose nanofibers were enzymatically treated with lauryl gallate in order to provide hydrophobic properties to the films surface. Both bleached and unbleached films improved significantly their water contact angle after the treatment. The results were especially surprising for the films made from bleached cellulose nanofibers, due to the absence of lignin moieties. Hence, a mechanism of hydrophobization was proposed for the films containing bleached cellulose nanofibers. The surface analysis of the treated films displayed different results. By one hand, lignin-containing films increased their roughness after the enzymatic grafting of lauryl gallate. By other hand, films made from fully bleached cellulose nanofibers reduced drastically the surface roughness. Therefore, the presence of lignin in the enzymatically treated cellulose nanofibers has a positive impact on the hydrophobic properties and a slight effect on the surface roughness.