Sustainable and high-performable nano-structured biopackaging materials

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ABSTRACT

Soy-protein isolate (SPI) film plasticized with different content of linear or branched additives (nanocellulose, xylan) and in the presence of glycerol and water were prepared using compression-moulding, and analyzed related to their structural, mechanical and water barrier properties. In addition, the influence of interface chemistry as well as biopolymer morphology and orinetation in mono- or multi-layer laminated film composites is shown.

Keywords: Soy-protein film, nanocellulose, modifications, cross-linking, multi-layer composite, barrier and mechanical properties.

1 INTRODUCTION

There are a number of drivers that are fuelling the growth in the bio-packaging market - from recent technological advances that are helping to bring down their cost and expand their range of properties - to the need to move away from petrochemical based materials and steer the plastics industry down to a more sustainable route. Bio-renewable polymers derived from pure feedstock represents an ecologically-friendly, biodegradable, cheap and compostable alternative. However, in terms of competing with many standard packaging materials, the properties are still not sufficient for certain applications. There is undoubtedly a gap in the market for biopackaging (non-paper and above all paper-based) that possesses good barrier (oxygen and water-vapor transition) and thermo-mechanical properties as well as suitable process-ability (thermoplastic behavior).

In the paper, few strategies for producing of highly-performed rigid or flexible biopackaging materials, being fabricated as mono- or even multi-layers coating films from renewable biopolymers (soy-protein-isolate SPI, being a by-product of the soybean oil industry [1,2], and/or xylan as the most common hemicelluloses extracted from the woody biomass), nontoxic linear or branched additives (acting as plasticizer and/or cross-linking agents), and differently pre-modified nano-cellulose (i.e. microfibrillar vs nanofibrillar celluloses, MFC vs. NFC, giving the strength and/or improve barrier properties) by using casting and compression molding techniques, is presented.

2 EXPERIMENTAL

2.1 Materials

The soy-protein isolate ProFam 974 (SPI) was purchased from ADM Specialties Division, Netherlands. It has a protein content of about 90% and 6% of moisture content. Glycerol (G) with Mw of 92.09 g/mol (CAS Number 56-81-5) was purchased from Sigma-Aldrich (Slovenia). All materials were used as received.

2.2 Mechanical Properties Determination

The tensile strength and elongation at break were determinate according to the ASTM D 638 with a Zwick/Roell ZO 10 at temperature of 22°C using strain rate of 0.025 sec^{-1} (velocity of deformation v = 50 mm/min) and pre-loading of 5 N. Films were conditioned in a controlled environment chamber at 20°C and 65% RH for a few weeks before testing.

2.3 Water Vapour Transmission Rate (WVTR) Determination

Water vapour transmission rate was determined in accordance with the ASTM E96-95 standard. Film samples (6.3 cm diameter disks that had been conditioned for 24 h) were fixed above aluminium cups containing 45 g of calcium chloride. The whole device was weighed and then placed in a climatically controlled chamber (32°C and 50 % RH). The cups were then weighed at regular time intervals and a linear relationship between the quantity of water transferred per unit air and time was obtained. Three independent determinations were carried out for each film sample and the mean of these three values is given as final result.

3 RESULTS AND DISSCUISON

3.1 Mono-layer compression-molded SPI films with/without inserted MFC/NFC or xylan as additives

The effect of **nanocellulose (MFC vs. NFC)** on mono-layer SPI film composites properties were studied (Fig. 1), showing on up to ~45% reduction of WVTR at simultaneous ~70% increase in tensile strength and reduction in elasticity in case of using $CaCl_2$ due ionic-interactions. Although the presence of MFC increase the WVTR, up to ~50% reduction of WVTR in case of using NFC and $CaCl_2$ was obtained, preserving (~15% reduction) of elasticity and an increase (~35%) of tensile strength.

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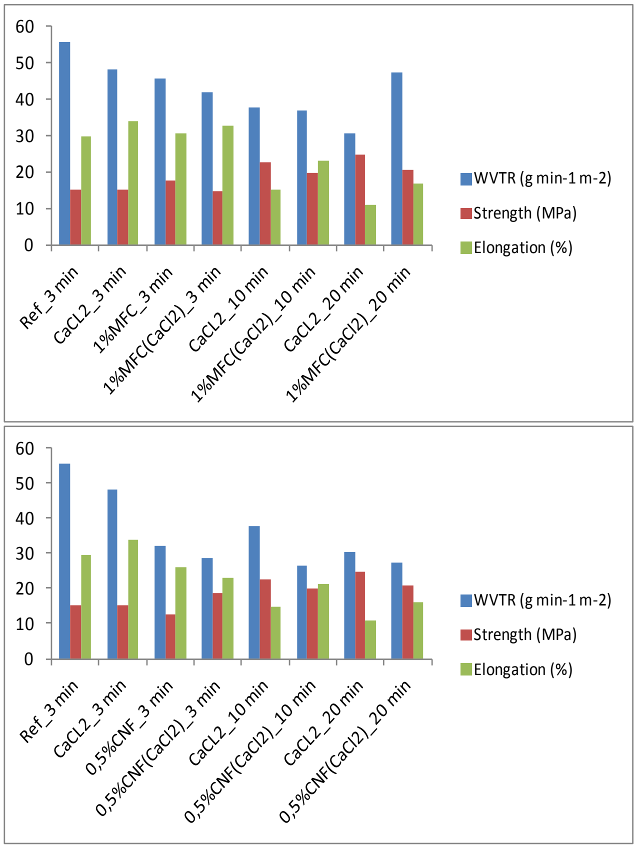


Fig. 1 SPI monolayer films contain MFC/NFC and/or $CaCl_2$

SPI films with incorporated **aldehyded-MFC** [4] of different concentrations show similar WVTR, tensile strength and elongation at break (data not show). The best WVTR performance was observed with MFC yielding 0.48 mmol/g of aldehyde groups, being likely related to the phenomenon of hemiacetal linkage that forms between aldehyde and hydroxyl groups of the MFC and SPI. In order to render the ionic interaction and improve MFC homogeneous distribution in SPI formulation, different **pH** conditions for films preparation were also investigated by regulating the SPI structure from globular (acid pH) to fibrilar (alkali pH) (Fig. 2). The presence of globular structures improves WVTR, but reduces the elasticity of the film. The incorporation of ald-MFC into SPI formulations at different pHs resulted in increased tensile strength, where the highest increase was at pH 7.5 (97.6%) and decreased elongation, where the highest decrease was at pH 4.5 where MFC forms aggregates.

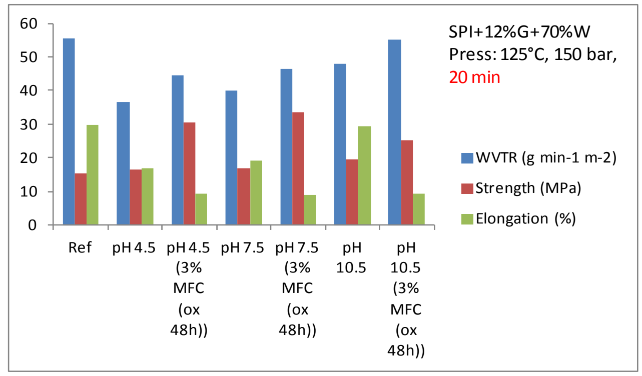


Fig. 2 SPI monolayer films prepared at different pH and with/without aldehyded-MFC (R-CHO)

SPI films with **native/acylated-NFC (R-CO-CH_3,** [4]**)** with higher surface area and partly hydrophobized groups (2.9%) were studied to improve barrier properties. The resulted composite SPI films (Fig. 3) exhibited an obvious improvement (~42% - ~49% reduction) of WVTR using 0.5%CNF or 3%NFC without significant changing of mechanical properties. Acyl-NFC prevented interaction among the SPI molecules and the immiscibility, provided more space for motion for the SPI segments or chains, thus no improvement in WVTR.

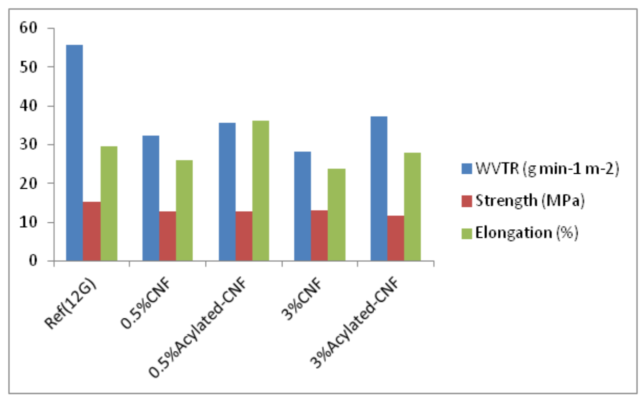


Fig. 3 SPI monolayer films contain native or acylated-NFC

SPI compounding with **native/aldehyded-Xylan** (branched polysaccharide, [3]) was shown (Fig. 4 and 5) to form chemical cross-linking accord. to Maillard reaction (coloration, Sch. 1), results to more rigid structure with decreased distance between the protein chains, thereby increasing the tensile strength (~43% - ~29%) and decreasing the elongation (~53% - ~44%), when films were compression molded at 90° - 125°C. By using the ald-xylan the results were not so significant. On the other hand xylan aldehyde groups are forming hemiacetals with remaining xylan hydroxyl groups (Sch. 2) during the solidification/sublimation process, without involving SPI chains, thus films retains its flexible nature with improved strength.

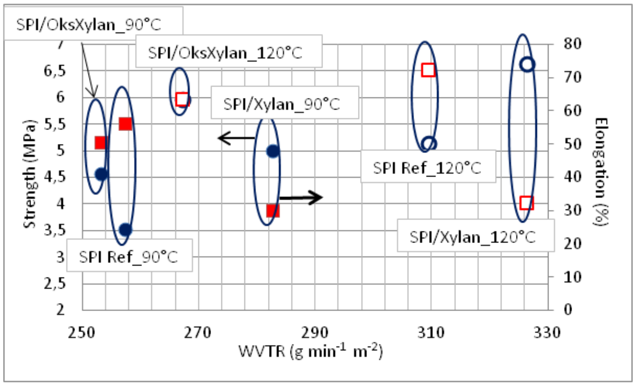
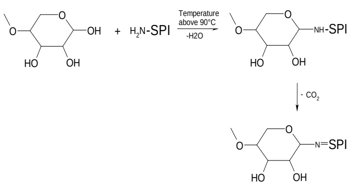
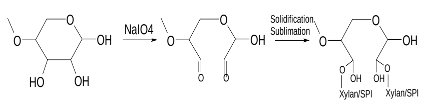


Fig 4. SPI films compression moulding at 90 and 125°C from freeze-dried SPI with/without xylan/ald-xylan.



Sch 1. Reactions involved in the cross-linking of SPI-xylan films during thermal compression molding



Sch 2. Reactions involved in the cross-linking of SPI-ald-xylan films during pre-freezing.

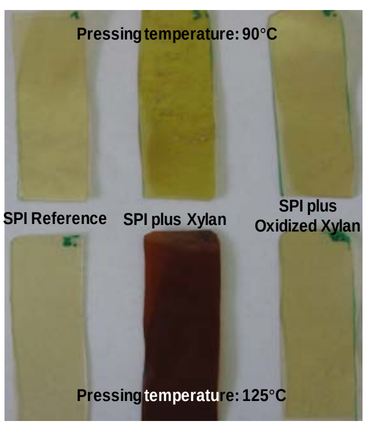


Fig. 5. Composite films after compression molding at 90°C or 125°C of pre-freeze-dried SPI composites with/ without native or ald-xylan.

3.2 Multi-layer compression-molded SPI films with/without MFC/NFC films as inter-layer

Multi-layer laminated SPI films (Fig. 6) (prepared without $CaCl_2$) resulted in ~65% reduction of WVTR without moderate changing of mechanical properties. The addition of $CaCl_2$ into films didn't bring an additional effect to WVTR, but decrease the elasticity.

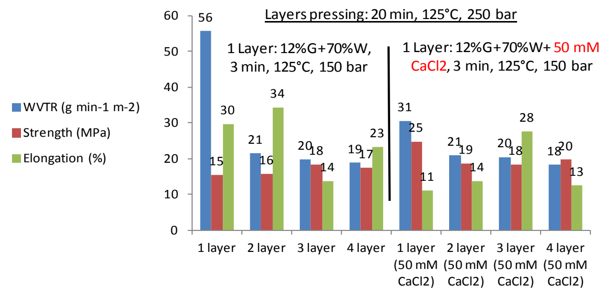


Fig. 6 SPI multi-layer laminated films prepared with/ without $CaCl_2$

SPI-SPI films **with MFC/NFC** (with $CaCl_2$) as **inter-layer** (Fig. 7) didn't bring additional improvement in WVTR. By using **acetylated-NFC** [4] **as inter-layer** ~70% reduction of WVTR was reached (Fig. 8).

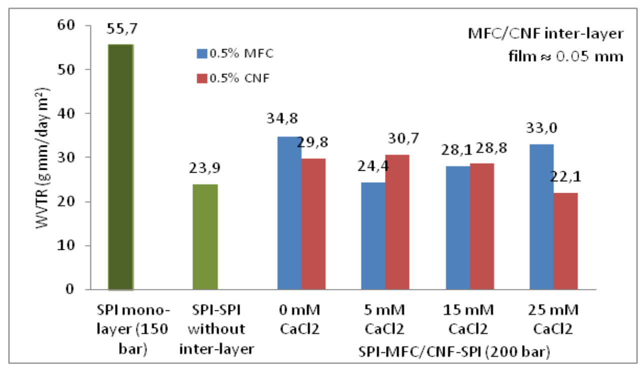


Fig. 7 SPI-SPI films with MFC/NFC as inter-layer

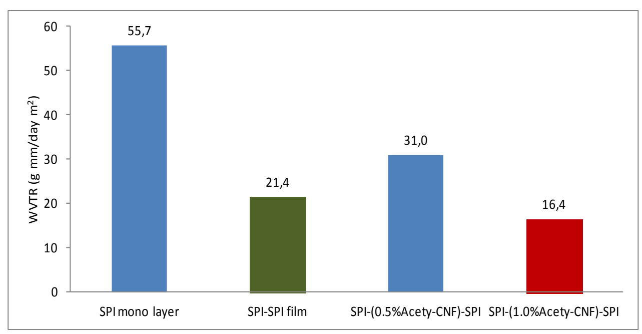


Fig. 8 SPI-SPI films with acetylated-NFC as inter-layer

4. CONCLUSION

The cross-linking (chemical or ionic using aldehyded-MFC, xylan or Ca-ions) of SPI film during lamination reduce (up to 45%) the WVTR, but obviously increase (45-70%) the tensile strength and reduce (up to 45%) the elongation, resulted to brittle films. Only the inclusion of NFC into SPI formulation reduce (up to 50%) the WVTR, preserving elasticity and tensile strength of SPI film.
Multi-layer laminated SPI films (prepared with Ca-ions) resulted to ~65% reduction of WVTR without moderate

changing of mechanical properties, being additionally reduced (~70%) to 14.6 g mm/day m^2 using few acetylated-NFC as inter-layer, showing very promising result.

4 ACKNOWLADGEMENT

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