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Short Communication

Extrusion of xylans extracted from corn cobs into biodegradable polymeric materials

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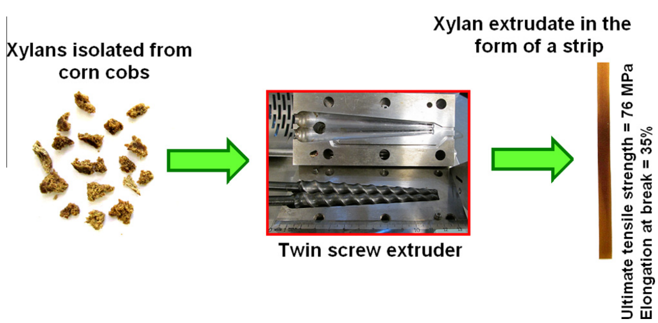
HIGHLIGHTS

- Xylans were isolated from corn cobs via alkaline extraction.
- Extracted xylans were conditioned to have different water contents.
- Conditioned xylans were fed to a twin screw extruder at different temperatures.
- Xylan extrudates were obtained at 27% water content and 90 °C extrusion temperature.
- Mechanical properties of xylan strips were superior to those obtained from PLA.

GRAPHICAL ABSTRACT



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ABSTRACT

Solvent casting technique, which comprises multiple energy demanding steps including the dissolution of a polymer in a solvent followed by the evaporation of the solvent from the polymer solution, is currently the main technique for the production of xylan based polymeric materials. The present study shows that sufficient water content renders arabinoglucuronoxylan (AGX) polymers extrudable, enabling the production of AGX based polymeric materials in a single step via extrusion, which is economically advantageous to solvent casting process for mass production. AGX polymers with water content of 27% were found to yield extrudates at an extrusion temperature of 90 °C. The extruded strips showed very good mechanical properties with an ultimate tensile strength of 76 ± 6 MPa and elongation at break value of 35 ± 8%, which were superior to the mechanical properties of the strips obtained from polylactic acid.

1. Introduction

Renewable biodegradable polymers and materials produced from these polymers are among the essential components of a sustainable environment. Hemicelluloses, which can be isolated from various lignocellulosic agricultural and forestry wastes, are one of the most abundant biopolymers in the nature where xylans are the most common type of hemicellulose (Ebringerova et al., 2005). The low cost of the raw materials from which xylans can be extracted makes xylans reasonable candidates as the base renewable biopolymers for the production of environmentally friendly polymeric materials. Corn cobs are lignocellulosic agricultural wastes, which are rich in arabinoglucuronoxylan (AGX) type of hemicelluloses (Ebringerova et al., 1992). Forming the polymer's backbone, the five carbon monosaccharide xylose is the main

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building block of the corn cob AGX where the xylose backbone is partially substituted with arabinose and glucuronic acid side groups (Ebringerova et al., 2005; Van Dongen et al., 2011).

In addition to their biodegradability, films based on xylan polymers are good oxygen barriers (Gröndahl et al., 2004; Höije et al., 2008), just like the films obtained from mannans (Hartman et al., 2006), another abundant type of hemicellulose. Furthermore, hemicellulose based films are potential lignocellulosic biorefinery products and their production can accompany the glucose production from the cellulosic fraction of the same lignocellulosic feedstock (Bahcegul et al., 2012).

The production method of a polymeric material has a significant impact on its cost and large scale production. Although solvent casting is a suitable method on laboratory scale, it is not a favorable method on an industrial scale compared to extrusion. Solvent casting process involves multiple steps including the dissolution of the polymer in a solvent followed by the evaporation of the solvent in order to obtain a polymeric film. On the other hand, extrusion processes does not need a solvent and the polymer is quickly transformed into the desired material making extrusion more industrially advantageous compared to solvent casting.

So far, solvent casting is the dominant method for the production of xylan based films (Hansen and Plackett, 2008; Mikkonen and Tenkanen, 2012). The present study explores the utilization of extrusion technique for the production of xylan based polymeric materials, which can lead to their large scale production in a more feasible manner compared to the current state of the art. AGXs with different water contents, which were extracted from corn cobs, were fed to an extruder operated at different temperatures in order to determine the necessary conditions for their successful extrusion into biodegradable materials, which were then characterized for their mechanical properties.

2. Methods

2.1. Extraction of AGXs from corn cobs

The isolation of AGX from corn cobs was conducted according to a previously reported procedure by Zilliox and Debeire (1998) with some modifications. Corn cobs, which were obtained from Hatay in Turkey, were milled to a particle size of less than 2 mm and 100 g of milled corn cobs were swelled in water at room temperature for 15 min. Following filtration, swelled corn cobs were suspended in 850 ml of 24% KOH solution at room temperature with magnetic stirring for two hours. The suspension was filtered with a filtering cloth and centrifuged at 5000 rcf in order to obtain an alkaline AGX solution. The AGX polymers in the alkaline solution were precipitated by the addition of a 2.5 L of acetic acid and ethanol solution (1:10 volumetric ratio of acetic acid to ethanol). The precipitated polymers were recovered from the suspension via a filtering cloth. The recovered polymers were partially solubilized in 200 ml of water and re-precipitated by the addition of 600 ml of ethanol. This step was repeated 3 times and finally the precipitated polymers were recovered and left to dry at room temperature. The AGX yield was calculated as 29% on the basis of the initial weight of corn cobs subjected to alkaline extraction.

2.2. Characterization of AGXs

The AGX polymers extracted from corn cobs were characterized for their xylose, arabinose, lignin and protein contents in addition to their molecular weights. For the determination of the xylose and arabinose content, the AGX polymers were hydrolyzed with sulfuric acid in two successive steps as described in the procedure reported by the National Renewable Energy Laboratory (NREL) (Sluiter et al., 2008). The hydrolysates were analyzed by high performance liquid chromatography (Thermo Scientific Finnigan Surveyor HPLC system equipped with a Transgenomics CARBOSep COREGEL-87P column, column temperature: 85 °C, flow rate: 0.6 ml/min, mobile phase: water). The xylose and arabinose contents of the AGX polymers were determined as 65% and 15%, respectively. The lignin content of the AGXs was determined by UV/Vis spectrophotometry according to the absorbance of the AGX solutions at 280 nm (Westbye et al., 2007). Samples were solubilized in 4% NaOH solution in order to ensure the complete solubilization of the polymers (Garcia et al., 2000). Alkali lignin was used as a standard. The lignin content of the polymers was determined as 12%. The AGXs had a protein content of 0.2% as determined via Kjeldahl method. Considering that the alkaline extracted corn cob AGX contains around 4% glucuronic acid (Garcia et al., 2000), the remainder of the AGX composition is likely made up of mainly glucose and galactose.

The molecular weight of the AGXs was determined via capillary viscometry. The concentration of the AGX solutions was between 2 and 10 mg/ml with 2 mg/ml increments. 4% NaOH solution was used as the solvent during the measurements (Garcia et al., 2000), which were conducted at 25 °C. Intrinsic viscosity was calculated as 0.0654 ml/mg and was used to calculate the molecular weight of the polymers via the Mark–Houwink equation ($K = 2.67 \times 10^{-4}$, $\alpha = 0.73$) (Eremeeva and Bykova, 1993) as 44,000 g/mol.

2.3. Extrusion of AGXs

A twin-screw, co-rotating extruder (Thermo HAAKE MiniCTW) with conical screws (Screw diameter: 4–15 mm, screw length: 109.4 mm) and two heating zones was used for the extrusion of AGX polymers. An important feature of this extruder is its capability to work with small amounts of material where 5 g of polymer is sufficient to obtain the desired extrudate. A ribbon die plate with a rectangular opening of 5 × 0.5 mm (width × length) was attached to the extruder in order to obtain the extruded material in the form of a strip. The strip coming out of the extruder was collected on a mini moving belt. The extrusion parameters, including extrusion temperature and screw speed, were controlled via a PC connected to the extruder by using the software supplied together with the extruder.

Prior to extrusion, AGXs were first conditioned at three different relative humidities (10%, 55% and 90%) for 24 h in order to obtain polymers with different water contents. For each batch of conditioned polymers, 3 extrusion temperatures (60 °C, 90 °C and 120 °C) were studied. The extrusions were performed at a screw speed of 50 rpm and 5 g of AGX polymers were manually fed to the extruder for each run. Each extrusion trial was conducted twice by using two different batches of AGX polymers. All parts of the extruder including the barrel, screws and the die were thoroughly cleaned before starting a new trial in order to eliminate any possible effect the residual AGX polymers left from previous runs might have on the new extrusion trial. Polylactic acid (NaturePlast PLI005) was also extruded in the same extruder at a screw speed of 50 rpm where extrusion temperature was set to 170 °C (Baouz et al., 2013).

2.4. Characterization of extruded strips

The strips obtained from the extruder were cut into smaller pieces with a length of 8 cm. 18 samples were tested for the determination of their mechanical properties. The samples were conditioned in a climatic chamber (MMM Medcenter Climacell 111) at 23 °C and 50% RH for 24 h prior to tensile testing. The atmospheric condition of the tensile testing room was also adjusted to the same