Production and Utilization of Hemicelluloses from Renewable Resources for Sustainable Advanced Products

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Publication date: 2011


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Production and Utilization of Hemicelluloses from Renewable Resources for Sustainable Advanced Products

PhD Thesis
Zsuzsa Sárossy

Abstract

Vast amounts of by-products are generated every year from agricultural crop production and hence great quantities of polysaccharides remain underutilized. The polysaccharides from agricultural by-products can be separated and used in the form of new materials. This thesis is devoted to the possibility of using hemicelluloses for special polysaccharide film applications in the packaging sector, starting from hemicellulose isolations from a side product of agricultural processes, hemicellulose characterization and assessing material properties and the potential use of hemicellulose films in later applications.

First, water-soluble hemicelluloses of rye bran were extracted with a high-temperature treatment combined with enzymatic starch removal. After the hot water extraction, non-soluble fibers and protein fractions were separated and the washed fiber fraction was further treated with alkali (NaOH) solution with different solid to liquid ratios. The ratio of arabinoxylans (~65%) and β-glucans (~25%) was similar in the water-extracted and alkali-extracted materials; however, their arabinose/xylose (Ara/Xyl) ratio differed. The alkali-extracted arabinoxylan was less substituted with an Ara/Xyl ratio of 0.35, while the water-extracted material had an Ara/Xyl ratio of 0.54.

In order to analyse the monosaccharide composition of the isolated hemicelluloses, a method based on gas chromatography-mass spectrometry analysis of acetylated methyl glycosides was developed. The derivatives of the monosaccharides, arabinose, glucose and xylose were studied in detail using 13C-labeled analogues as internal standards for identification and quantitative analysis. The electron impact-induced fragmentation of all the studied monosaccharides was studied and quantification was made using extracted fragment ion pair (unlabeled and labeled monosaccharide fragment) intensities. Using the intensity ratios obtained from the ion chromatograms, accurate quantification of monosaccharide constituents from selected hemicelluloses was demonstrated.

The effect of co-extracted mixed linkage β-glucans on films cast from the isolated rye hemicelluloses was studied. Water-extractable mixed linkage β-glucans (BG) were isolated from oat bran using a similar process as was used for isolation of rye hemicelluloses. The β-glucan content of the rye hemicellulose isolate was reduced to less than 5% by a selective lichenase treatment. The material properties of films prepared from the rye hemicellulose isolate and lichenase-treated rye hemicellulose (WE-AX) as such, or with varying amounts of added BG (20:80; 50:50; 80:20 ratios) were studied. Prior removal of β-glucan from the isolate decreased the tensile strength of the films significantly as well as the elongation at break. Addition of BG to the purified WE-
AX resulted in an increase in the tensile strength and elongation at break of the films. In contrast, the presence of BG had no clear effect on the oxygen permeability of the films. Both pure rye WE-AX and pure BG films showed excellent oxygen barrier properties (0.9-1.0 cm³·µm/m²·d·kPa). However, the water vapour permeability increased with addition of increasing amounts of BG to WE-AX. Considering the mechanical and barrier properties of the films, it was shown that higher β-glucan contents have positive effects when practical applications of cast arabinoxylan-β-glucan films are considered.

In order to improve the mechanical and barrier properties of rye arabinoxylan films, nanocomposite films of arabinoxylan and a fibrous nanoclay (sepiolite) were prepared. The films contained 2.5 – 10% added nanoclay and showed high transparency, especially with lower sepiolite contents (2.5 and 5%). The nanoparticles were well embedded in the arabinoxylan matrix as shown by scanning electron microscopy. FTIR (Fourier transform infrared) spectroscopy provided some evidence for hydrogen bonding between sepiolite and the arabinoxylan matrix. Mechanical testing showed greatly improved tensile strength and Young’s modulus in the nanocomposite films. However, unlike layered nanoclays, addition of sepiolite fibers did not reduce the oxygen permeability of reinforced films.