Notes

Gas-Phase Surface Fluorination of Arabinoxylan Films

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1. Introduction

Almost 40% of all plastics are used as packaging,[1] which is often a short time application. The use of plant biopolymers to produce plastic materials has several advantages. In addition to their being a renewable resource, the product may after use be composted, recycled, or incinerated with minimal environmental impact.[2]

Hemicelluloses are the second most abundant plant biopolymers on earth.[3] They are heterogeneous polysaccharides whose composition varies between different plant species. The primary hemicellulose in hardwood is glucuronoxylan[4] and in annuals, such as barley, is arabinoxylan. Arabinoxylan contains a backbone of β-(1→4)-linked D-xylopyranosyl residues with α-linked L-arabinofuranose units at positions C3 and/or C2.[5]

New methods have been developed for extracting xylan from wood and annual plants,[6−15] and interest in xylan-based materials is increasing. Plasticized films made of aspen glucuronoxylan have low oxygen permeability[16] and thus may have a potential as food packaging materials. It has recently been shown that unplasticized barley husk arabinoxylan films have good mechanical properties.[17] Arabinoxylan films have low oxygen and carbon dioxide permeability, but, owing to the hydrophilic character of arabinoxylan, the water vapor permeability is high and the gas barrier properties become poorer when the films are exposed to moisture.[18]

The aim of this study was to evaluate the possibility of making barley husk arabinoxylan films less hydrophilic by modifying the surface with trifluoroacetic anhydride.

2. Experimental Section

2.1. Materials. The arabinoxylan used in this study was isolated from barley husks by alkali extraction after delignification with sodium chlorite ($NaClO_2$). The separation procedure is described elsewhere.[17] The extracted fraction was further treated with $NaClO_2$ and with Subtilisin A from Megazymes and Termamyl Ultra 300L and amyloglucosidase AMG 300L from Novozymes. The extract was then precipitated in ethanol, dialyzed, and freeze-dried. The distribution of neutral sugars was 79.9% xylose, 15.5% arabinose, and 4.5% glucose. The xylose-to-arabinose ratio was 4.52, and the weight-average molecular weight determined using size exclusion chromatography in an aqueous system was 39 100 g/mol. Trifluoroacetic anhydride (TFAA) (99%) was purchased from Sigma-Aldrich, Sweden.

2.2. Film Formation. Films were prepared by mixing 1 g of arabinoxylan and 35 mL of deionized water during magnetic stirring at 95 °C for 15 min. The solutions were poured onto Petri dishes, and films were allowed to form upon drying at 23 °C and 50% relative humidity (RH). The lower side was used for the surface modification studies.

2.3. Fluorination. The arabinoxylan films were dried in an oven at 45 °C for 24 h, and all glass equipment was dried at 130 °C for 2 h prior to use. 2 × 2 cm pieces of the dried films were placed in a glass container coupled via glass tubing and a turning vault to a round-bottomed beaker containing 5 mL of TFAA. The container was evacuated with a vacuum pump for 5 min and filled with nitrogen gas for 3 min three times before the last evacuation, and the vault was opened in order to allow the TFAA to evaporate and react with the film. For infrared (IR) spectroscopy, smaller samples were used and the exposure times were longer to obtain samples with high amounts of fluorine.

2.4. Electron Spectroscopy for Chemical Analysis. The fluorine concentration of all sample surfaces was determined with electron spectroscopy for chemical analysis (ESCA) ~24 h after modification. Both wide-scan and high-resolution spectra were obtained. The samples were analyzed using a Quantum 2000 scanning ESCA microprobe from Physical Electronics. The area analyzed was 500 × 500 μm and the takeoff angle was 45°, which resulted in a sampling depth of 4−5 nm. The X-ray source used was an Al Kα (1486.6 eV).

2.5. Infrared Spectroscopy. Pieces of films were placed in a vibrating mill from Perkin-Elmer and ground to a fine powder. 2−5 mg of powder was mixed with 200 mg of potassium bromide (KBr) and pressed to a tablet. IR spectra were obtained on a System 2000 FT-IR from Perkin-Elmer. Spectra in the 4000−700 cm^{-1} interval were detected with a TGS detector. To obtain attenuated total reflectance IR (ATR-IR) spectra, films were placed on both sides of a germanium crystal. A System 2000 FT-IR from Perkin-Elmer was used, and the spectra were detected by an MCT detector.

2.6. Dynamic Absorption and Contact Angle Tester. For the dynamic absorption and contact angle tester measurements (DAT), the samples were placed on a sample holder and inserted into a DAT1100 from FIBRO system AB 24 h after modification. Ten 4 μL water droplets were used for each sample. The average of the contact angles from 6 to 10 s after the droplet was applied was used to calculate a mean value.

2.7. Equilibrium Moisture Content. The equilibrium moisture content at 50% RH and 23 °C was measured gravimetrically on a Mettler AE260-DR balance and calculated as the weight of water in the sample at equilibrium compared to the total weight. The films were allowed to reach equilibrium before they were weighed, dried in an oven at 130 °C for 24 h, and weighed again.

3. Results and Discussion

3.1. Fluorination. The arabinoxylan films were homogeneous and transparent but rather brittle. Figure 1 shows the reaction that takes place between the TFAA and the hydroxyl groups of the arabinoxylan.[19,20]

The fluorine content at the film surface, as studied by ESCA, shows how far the reaction has proceeded. Figure 2 shows ESCA wide scans of the unmodified arabinoxylan film and of

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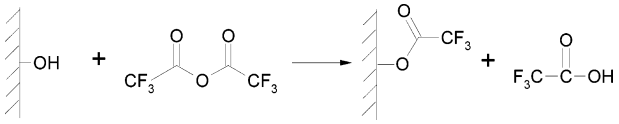

Figure 1. Reaction of arabinoxylan with TFAA.

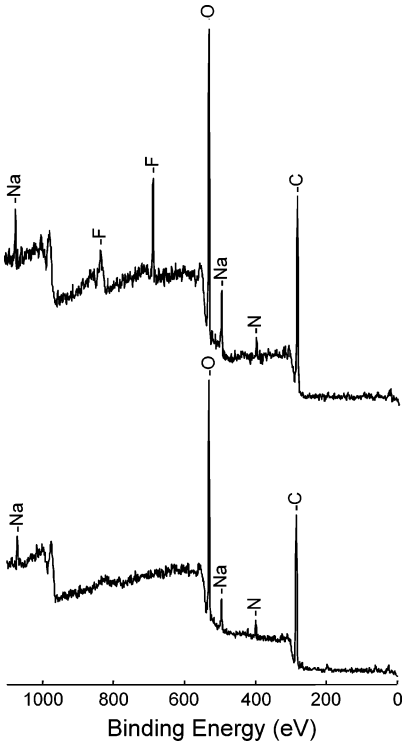

Figure 2. Electron spectroscopy for chemical analysis wide scans of unmodified arabinoxylan film (bottom) and of fluorinated arabinoxylan film (top).

a modified arabinoxylan film. The surface of the unmodified film contains mainly carbon and oxygen, but there are also small peaks of sodium and nitrogen. The sodium comes from the extraction process, where NaOH is used, and can act as a counterion to the uronic acid groups of the arabinoxylan. The nitrogen probably originates from proteins that are enriched at the surface during film formation. Proteins have been observed to migrate to the surface of starch films prepared by casting from aqueous solution.[21] The modified film has additional fluorine peaks, which verifies that the TFAA has reacted with the arabinoxylan film surface.

Figure 3 shows ESCA narrow scans of the C 1s peak of the unmodified arabinoxylan film and of a modified arabinoxylan film.

The peaks in the scan of the unmodified film, from right to left, correspond to carbon bound only to carbon and hydrogen (C1), carbon with one bond to oxygen (C2), and carbon with two bonds to oxygen (C3). In pure arabinoxylan, each monosaccharide unit contains four C2 and one C3. The C1 peak originates from impurities at the surface, such as proteins and lignin. In the ESCA narrow scan of the C 1s peak of a fluorinated arabinoxylan film two additional peaks at higher binding energy can be seen, correlating to carbon with three bonds to oxygen (C4) and carbon bound to fluorine (C5). One C4 and one C5 are added for each TFAA molecule that reacts with the surface, and these two peaks are of the same size in the spectra.

The fluorine content at the surface as a function of the reaction time is seen in Figure 4. After 2 min, the surface contains ~1% fluorine. After 2 h, the fluorine content is ~7%. The reaction kinetics is strongly dependent on the size of the sample that is modified, as a consequence of a greater amount of water being present in a larger sample, even after drying. The reaction is inhibited by the reaction of water with TFAA to form trifluoroacetic acid.

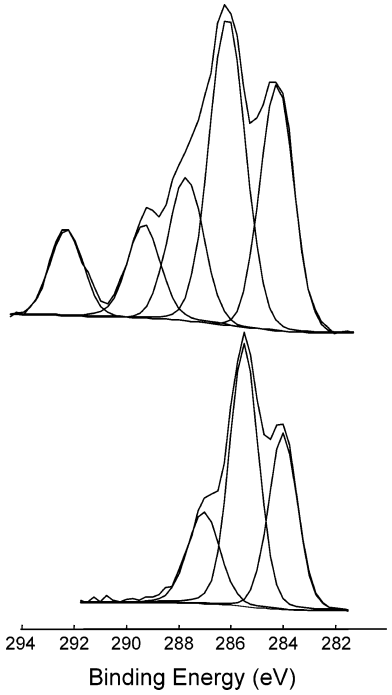

Figure 3. Electron spectroscopy for chemical analysis narrow scans of the C 1s peaks of unmodified arabinoxylan film (bottom) and of fluorinated arabinoxylan film (top).

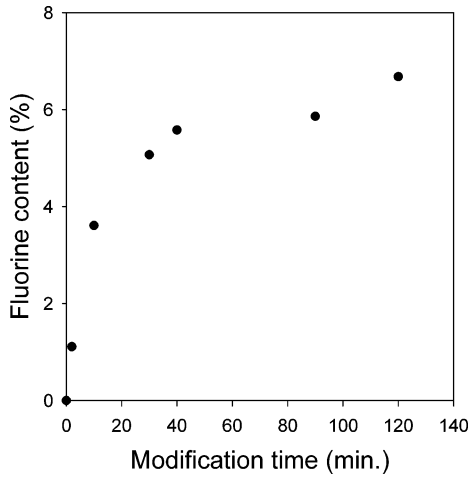

Figure 4. Fluorine content at the surface of the arabinoxylan films, determined by ESCA, as a function of the reaction time.

It can be concluded from the ESCA analysis that a reaction does take place, but it is not obvious whether it is a surface or a bulk modification. Two different IR spectroscopy techniques were used to evaluate this. Arabinoxylan films ground and pressed to tablets with KBr were used to see whether there was a detectable difference between the samples when looking at the bulk of the samples (see Figure 5). The β-1,4-glycosidic bonds between the monosaccharide units absorb strongly at 1200−990 cm^{-1},[22] and as this peak is proportional to the amount of sample, it was used to normalize the spectra. No difference could be observed in the carbonyl region between the samples.

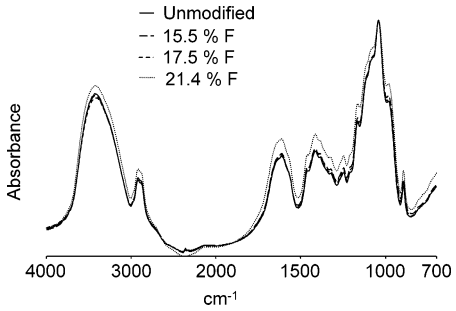

Figure 5. Infrared spectra of unmodified and fluorinated ground arabinoxylan films.

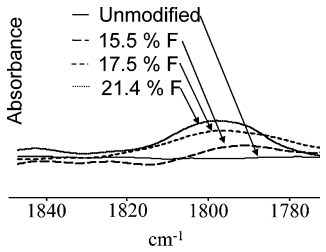

Figure 6. Attenuated total reflectance infrared spectra of unmodified and of fluorinated arabinoxylan films.

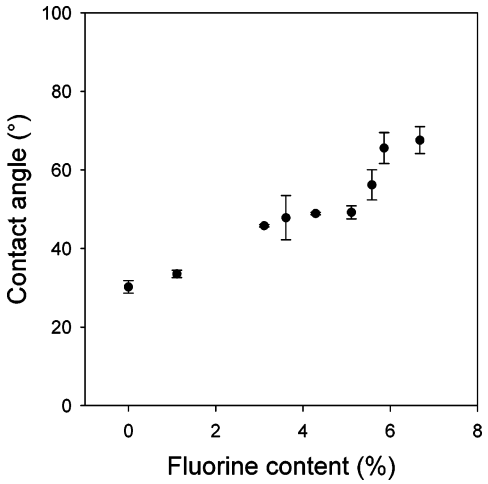

Figure 7. Contact angle of the arabinoxylan films as a function of the fluorine content at the surface.

However, a comparison of the spectra in the ATR-IR measurement shows that a small peak appears close to 1800 cm^{-1} for the fluorinated samples (see Figure 6). The trifluoroacetate group of ethyl trifluoroacetate absorbs radiation at 1788 cm^{-1},[23] and this peak corresponds to the trifluoroacetate that has reacted with the arabinoxylan. The peak height increases with an increasing amount of fluorine at the surface and shows that this is indeed a surface modification and not a bulk reaction.

3.2. Contact Angle. The contact angles of the unmodified and fluorinated films were measured using DAT in order to evaluate whether the modification makes the films less hydrophilic. Figure 7 shows the contact angle as a function of the fluorine content. The unmodified arabinoxylan film has a contact angle of 30°, which is quite hydrophilic. The contact angle increases considerably with an increasing amount of fluorine at the surface to 70° for an arabinoxylan film with 7% fluorine. Thus, the modification did meet the expectation of making the films less hydrophilic.

3.3. Equilibrium Moisture Content. The equilibrium moisture content of the films as a function of the amount of fluorine at the surface was measured (see Figure 8). The equilibrium moisture content at 50% RH decreases somewhat with increasing fluorine content. The unmodified arabinoxylan films have a moisture content of 18% at equilibrium, and a sample with 7% fluorine contains 12% moisture.

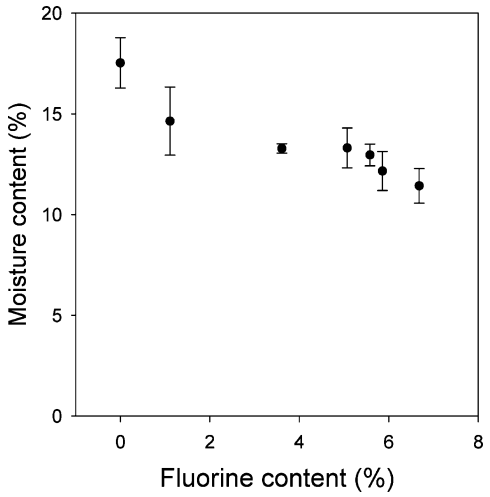

Figure 8. Equilibrium moisture content of the arabinoxylan films at 50% RH and 23 °C as a function of the fluorine content at the surface.

4. Conclusion

Arabinoxylan films were made less hydrophilic by surface modification with TFAA in the gas phase.

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