

MICROFIBRILLATED CELLULOSE REINFORCED GALACTOGLUCOMANNAN AND ARABINOXYLAN FILMS

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Keywords: arabinoxylan, galactoglucomannan, microfibrillated cellulose, composite films

Abstract

Novel sustainable composite films were prepared from spruce galactoglucomannans and rye arabinoxylans reinforced with microfibrillated spruce wood cellulose (MFC). The tensile strength of films significantly increased with the addition of MFC. The moisture uptake decreased and the relative humidity of softening of the films, studied with dynamic mechanical analysis, increased when MFC was added. X-ray diffraction studies were done by subtracting the scattering of x-rays due to MFC from the measured diffraction patterns, to show that the degree of crystallinity of mannan and xylan in the films was independent of the presence of MFC.

1 Introduction

Hemicelluloses, including xylans and mannans, are the most abundant plant polysaccharides other than cellulose. They are biosynthesized in large quantities in the majority of trees and terrestrial plants. In spite of their abundance, the industrial utilization of hemicelluloses is minor in comparison with the use of starch and cellulose. In many lignocellulosic refining processes, hemicelluloses are partly degraded, they are removed and burnt, or further used as feed raw material. However, methods for separation and isolation of high molar mass hemicelluloses have been developed. Hemicelluloses can be extracted from plant material with alkali; parts of them are extracted also with water. The amount of potential raw material from forestry and agricultural side streams is significant and researchers are currently aiming at finding potential uses for it. Unlike starch, hemicelluloses are not digested by humans but function as a dietary fiber. Potential applications for hemicelluloses include paper making, biodegradable packaging materials, coatings, hydrogels, absorbents, and emulsifiers. Development of bio-based and biodegradable films from hemicelluloses to replace conventional synthetic packaging is a highly interesting research area [1].

We have recently studied the preparation of films from spruce galactoglucomannans (GGM) [2] and rye arabinoxylans (rAX) [3] as such and reinforced with microfibrillated softwood cellulose (MFC), to obtain sustainable plant-derived composite materials.

2 Materials and testing methods

2.1 Materials

GGM was obtained from process water of a Finnish pulp mill according to Willför et al. [4]. High molar mass rye endosperm arabinoxylan (rAX) was purchased from Megazyme (Wicklow, Ireland). MFC was prepared by high-pressure homogenization of partially carboxymethylated (for GGM films) or enzymatically pretreated (for rAX films) commercial sulfite softwood-dissolving pulp (Domsjö Fabriker AB, Sweden) followed by ultrasonication and centrifugation [5]. Glycerol (Rectapur) was from Prolabo, France.

2.2 Preparation of films

Films were prepared from GGM and rAX with and without the addition of MFC. The hemicellulose:MFC weight ratio used was 85:15. GGM films were plasticized with 40% (w/w of GGM) glycerol. GGM and glycerol were dissolved in de-ionized water at 80 °C, after which MFC was added. Both the GGM solution and GGM-MFC suspensions were homogenized with three passes through a high pressure homogenizer (Microfluidizer M-110EH, Microfluidics Corp., USA) with an operating pressure of 1650 bar. The samples were degassed under vacuum for two hours, cast into teflon plates, and dried at room temperature. The rAX solution and rAX-MFC mixture were heated under magnetic stirring at 60 °C and homogenized using an Ultra-Turrax (Ika-Werke, Staufen, Germany) at 9,500 rpm for 10 min, cast into Teflon-coated Petri dishes, and dried at 23°C and 50% RH. The thickness of the films was approximately 20–40 µm.

2.3 Tensile properties

The tensile strength, elongation at break, and Young's modulus of the films were determined at 23 °C and 50% RH using an Instron 4465 universal testing machine with a load cell of 100 N. The initial grip distance was 50 mm and the rate of grip separation 5 mm/min. Two films of each type and five to six replicate specimens from each film were measured. The thickness of the specimens was measured with a micrometer (Lorentzen & Wettre, Sweden) at three points and an average was calculated.

2.4 Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) was carried out using a Perkin-Elmer DMA 7e (PerkinElmer Corp., USA). Pieces of films (2 mm × 15 mm × 20 µm) were first conditioned at 0% RH and then scanned in a range of 1% – 90% RH at a temperature of 30 °C. The relative humidity was controlled with a Wetsys humidity generator (Setaram Instrumentation, France). The static load was adjusted to be equal to 120% of the dynamic load, the amplitude was set to be constant at 5 µm, and a frequency of 1 Hz was applied. The storage modulus (E') was recorded using a Pyris DMA 28 software (PerkinElmer Corp., USA).

2.5 Water sorption

A DVS Intrinsic sorption microbalance (Surface Measurement Systems, Alperton, Middlesex, UK) was used in order to collect water sorption isotherms of rAX films. The experiments were carried out in duplicate at 25 °C and RH values from 0 to 90%. The sample was hydrated stepwise in 10% RH steps by equilibrating the sample weight at each step.

2.6 X-ray diffraction

Wide angle x-ray scattering measurements were carried out in the perpendicular transmission geometry using Cu K α 1 radiation. A setup with an x-ray tube (from Rigaku Corp., Japan for GGM films and from PANalytical, The Netherlands, for rAX films) and a MAR345 image plate detector (Rayonix, USA) was used. The recorded two dimensional diffraction patterns were averaged to one dimensional diffraction intensity profiles. The scattering of x-rays due to MFC was subtracted from the measured diffraction patterns to obtain the degree of crystallinity of mannan and xylan in the films.

3 Results and discussion

Film formation was successful from rAX as such, but the addition of plasticizer was necessary to obtain cohesive films from GGM. MFC was added as a reinforcement to strengthen the films. The addition of MFC had a clear effect on the mechanical properties of the films, as the tensile strength and Young's modulus of both GGM and rAX films were significantly higher when MFC was used (Table 1). The tensile strength of rAX films was rather high (64 MPa) even without cellulose reinforcement. With MFC, the tensile strength of rAX films was as high as 95 MPa. GGM has lower molar mass than rAX, and a relatively large amount of external plasticizer is necessary for film formation. This also leads to lower tensile strength of GGM-based films in comparison to rAX films. The elongation at break of both GGM and rAX films slightly decreased due to the addition of MFC, but taking the standard deviations into account, the effect was not significant (Table 1). GGM-based films were semicrystalline with a degree of mannan crystallinity of about 25%, while rAX films were amorphous (Table 1). The addition of MFC did not significantly affect the crystallinity of hemicelluloses in the films.

Film	Tensile Strength [MPa]	Elongation at break (%)	Young's modulus (MPa)	Crystallinity (%)
GGM/40gly	13.7 \pm 5	4.2 \pm 0.6	743 \pm 223	25 \pm 3
GGM:15MFC/40gly	19.3 \pm 6	3.6 \pm 0.8	909 \pm 350	25 \pm 5
rAX	63.8 \pm 6	12.4 \pm 5	1830 \pm 365	0
rAX:15MFC	95.1 \pm 19	10.9 \pm 4	2520 \pm 474	0.5 \pm 2

Table 1. Tensile strength, elongation at break, Young's modulus, and crystallinity of hemicelluloses in films from spruce galactoglucomannans (GGM) plasticized with 40% glycerol (gly) (w/w of GGM) and rye arabinoxylans (rAX) with and without microfibrillated cellulose (MFC) as reinforcement at hemicellulose:MFC weight ratio of 85:15.

The relative storage modulus (E'), studied with DMA, indicates the stiffness of the films. As expected, increase in the relative humidity caused softening of rAX films (Figure 1). However, the addition of MFC clearly increased the RH of softening of the films. At 90% RH, the MFC-reinforced rAX films maintained approximately 50% of their original stiffness, while the corresponding value for plain rAX films was 30%. The difference can be at least partially explained by decreased moisture uptake of the films due to MFC addition, leading to decreased plasticization by water (Figure 1).

4 Conclusions

MFC clearly acted as reinforcement increasing the mechanical performance of GGM and rAX films. The tensile strength and Young's modulus of films increased and moisture-sensitivity decreased due to the addition of MFC. At the same time, the flexibility of films and crystallinity of hemicelluloses in the films were not affected. Mannans and xylans are

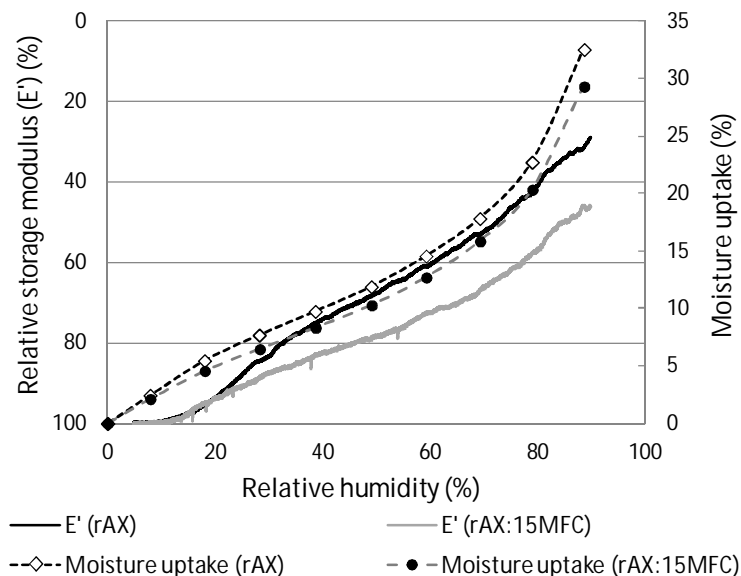


Figure 1. Relative storage modulus (E') and moisture uptake of rye arabinoxylan (rAX) films reinforced with microfibrillated cellulose (MFC).

potential future biorefinery products to be developed as sustainable materials to replace conventional petroleum-based plastics. The properties of mannan- and xylan-based films can be further enhanced by combining them with MFC.

5 Acknowledgements

The Academy of Finland and Formas are gratefully acknowledged for funding through the Wood Wisdom-Net Programme. Wallenberg Wood Science Center is acknowledged for funding JSS. COST Action FP0901 is thanked for funding of the Short Term Scientific Mission for KSM to Innventia, Sweden. We thank Prof. Stefan Willför (Åbo Akademi, Finland) for the GGM sample, Mikael Ankerfors and Tom Lindström (Innventia, Sweden) for the MFC sample, and Åsa Blademo (Innventia) for performing the homogenization of GGM and MFC.

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