Colloids and Surfaces A: Physicochem. Eng. Aspects 506 (2016) 600–606

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Surface properties of xylan and xylan derivatives measured by inverse gas chromatography

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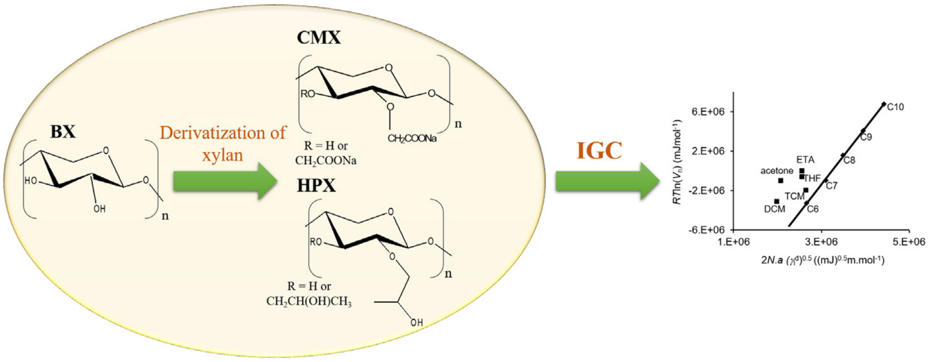
HIGHLIGHTS

- Carboxymethyl and hydroxypropyl xylans were analysed for their surface properties.
- The dispersive component of the surface energy decreased in the order: BX > CMX > HPX.
- CMX showed a lower prevalence of the Lewis acidity over the Lewis basicity than BX.
- HPX (with a high substitution degree) showed a perfectly Lewis amphoteric character.
- Results may have an interest for the xylans application in composites/barrier materials.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 9 May 2016
Received in revised form 1 July 2016
Accepted 3 July 2016
Available online 5 July 2016

Keywords:
Inverse gas chromatography
Wood xylan
Xylan derivatives
Surface energy
Lewis acid-base character

ABSTRACT

Xylan (the most common hemicellulose in wood and annual plants) and xylan derivatives have a very wide field of uses for which physico-chemical surface properties play an important role (e.g. in composites or barrier materials). In the present work, for the first time, inverse gas chromatography (at infinite dilution conditions) was used to assess the surface properties of xylan and xylan derivatives. Firstly, carboxymethyl xylan (CMX) and hydroxypropyl xylan (HPX) have been synthesized from commercial xylan (BX) and the presence of substituent groups confirmed by infrared spectroscopy and ^{1}H NMR. Then, the modified and original xylans were analysed for their dispersive component of the surface energy ($\gamma_s{}^d$) and Lewis acid-base properties. It was found that carboxymethylation and hydroxypropylation decreased significantly the $\gamma_s{}^d$ value of xylan: from 47.6 mJ m^{-2} in BX to 33.0 mJ m^{-2} and 23.5 mJ m^{-2} in CMX and HPX, respectively. As for the Lewis acid-base properties, HPX showed a perfectly amphoteric behaviour while the surfaces of unmodified xylan and CMX showed a prevalence of Lewis acidic character over the Lewis basic character, being, however, the surface of CMX less acidic than that of the original xylan. These results were interpreted in terms of the effect of the presence of the new substituent groups in the xylan backbone.

1. Introduction

Hemicelluloses are the second most abundant natural polymer after cellulose, comprising about 25–35% of most plant materials, forest and agricultural residues [1–3]. Xylans are the most

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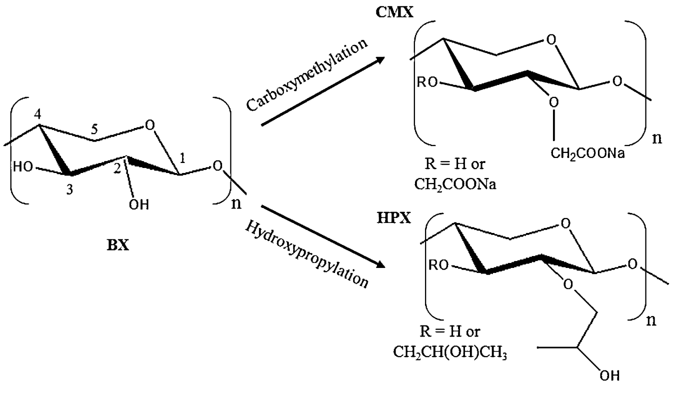
http://dx.doi.org/10.1016/j.colsurfa.2016.07.006
0927-7757/

common hemicellulose in wood, as well in annual plants such as grasses, cereals, and herbs [4], representing about 10–35 wt% of hardwoods (e.g. eucalypt, maple, birch) and 10–15 wt% of softwoods (e.g. spruce, pine and cedar) [5]. This polysaccharide is formed by β-(1 → 4)-linked D-xylopyranose (D-Xyl*p*) monomer units, being, however, the chemical structure dependent on the xylan source [6]. The main xylan in hardwood species is *O*-acetyl-4-*O*-methylglucuronoxylan while in softwood species is arabino-4-*O*-methylglucuronoxylan. The former is constituted by a main chain of D-Xyl*p* units with a few 4-*O*-methylglucuronic acid (MeGlcA) groups attached to the C-2 position of the xylan backbone and several hydroxyl groups substituted by acetyl groups at the C-2 and/or C-3 positions (about one MeGlcA group per 10–23 xylose units and 4–7 acetyl groups per 10 xylose units) [7–9]. The latter is a non-acetylated xylan where D-Xyl*p* units are branched with MeGlcA groups and α-L-arabinofuranose units [7].

Xylans have a very wide field of uses and their potential can be enhanced by chemical derivatization. They have been applied in the production of bioethanol, xylitol and xylooligosaccharides [3,6,10,11], as well as in films with low oxygen permeability [12–14], composites [15,16], hydrogels [17], surfactants [18], as paper additives and flocculation aids [19,20], antimicrobial agents [20] and coating color components [21]. In particular, they play an important role in pulping and papermaking processes as they increase the yield of the pulping process and improve the paper mechanical properties. However, the recent increasing demand for α-cellulose (dissolving pulp) and the production of nanocellulose open new possibilities for hemicelluloses production [21]. Moreover, the increasing demand for advanced renewable materials and green technologies has led researchers to focus their work in the plant biomass and value-added chemicals obtained from that. Abundant natural-based polymers, such as cellulose and hemicelluloses are, thus, of obviously high interest for both the scientific researchers as well as for the industry partners.

In this context, surface properties of xylans and modified xylans are an important issue to consider in order to: (a) determine the influence of added functional groups in xylan's modification; (b) predict and optimize their compatibility with other polymers in the composites production; (c) expand their use in films for packaging and barrier materials. Inverse gas chromatography (IGC) is an appropriate tool to assess the surface properties of powdered solid materials, such as xylans, not possible to assess adequately, for instance, by classical contact-angle measurements (due to associated problems like porosity, roughness, surface heterogeneity). IGC enables to obtain the dispersive component of the surface energy, specific interactions (non-dispersive) with polar probes, Lewis acid-base character of the surface, surface nanoroughness parameter, Flory-Huggins interaction parameter [22–25], among other properties. This technique has been widely used for the study of cellulose and lignocellulosic materials [22] but, to our knowledge, it has never been reported before for the study of xylans of any type.



Scheme 1. Schematic representations of xylan, carboxymethyl xylan (CMX) and hydroxypropyl xylan (HPX) considered in the present study.

In the present work, a commercial beechwood xylan, and two modified xylans produced from commercial xylan by carboxymethylation and hydroxypropylation (Scheme 1) were analysed, for the first time, for their surface properties by inverse chromatography. Results of this study revealed significant differences between the several materials, namely for their dispersive component of the surface energy as well as for their Lewis acid-base properties.

2. Materials and methods

2.1. Materials

Beechwood xylan (BX) (Sigma-Aldrich, St. Louis, MO, USA) was used as the xylan source. Deuterium oxide (99.9 at.% D), (±)-propylene oxide (ReagentPlus 99%) and sodium monochloroacetate were purchased from Sigma-Aldrich (St. Louis, MO, USA). Sodium hydroxide (Pronalab, Lisbon, Portugal), hydrochloric acid, 2-propanol (Merck, Darmstadt, Germany), acetic acid, ethanol (Sigma-Aldrich, St. Louis, MO, USA), sulphuric acid (Panreac, Barcelona, Spain) and acetone (Scharlau, Barcelona, Spain), were used as reagent-grade chemicals. All probes for IGC analysis were of chromatographic grade and were used as received (Sigma–Aldrich, St. Louis, MO, USA).

2.2. Derivatizations of xylan

2.2.1. Carboxymethylation

Carboxymethyl xylan (CMX) synthesis was carried out according to a method reported by Petzold et al. [26]. Briefly, 5 g of BX (37.8 mmol of anhydroxylose units (AXU)) was dissolved in 25 mL of 25% aqueous sodium hydroxide solution followed by the addition of 35 mL of 2-propanol. The mixture was stirred for 30 min at 30 °C. Then, 4.39 g (37.8 mmol) of sodium monochloroacetate was added and the temperature raised to 65 °C for 70 min. The reaction mixture was neutralized with diluted acetic acid, and then the CMX was precipitated, filtered and washed with ethanol, and finally dried at room temperature.

2.2.2. Hydroxypropylation

Hydroxypropyl xylan (HPX) synthesis was carried out according to the method used by Laine et al. [21]. Briefly, 13 g of 50% aqueous sodium hydroxide was added to 3.25 g of BX dispersed in distilled water (16.3%, w/w) and the mixture vigorously stirred in a pressure reactor. 7.6 mL of cooled propylene oxide was then added and the reaction mixture heated at 50 °C for 40 h. The reaction mixture was neutralized with 1 M hydrochloric acid solution, and then the HPX was precipitated by adding acetone. After washing, the HPX was freeze dried.

2.3. Characterization of xylans

2.3.1. Neutral sugar analysis

The determination of the neutral sugars composition of BX was undertaken after Saeman hydrolysis (treatment with 72% H_2SO_4 at 20 °C for 3 h, followed by 2.5 h hydrolysis with 1 M H_2SO_4 at 100 °C). The released neutral monosaccharides were determined as alditol acetate derivatives by gas chromatography [27] using a Varian 3350 gas chromatograph equipped with a FID detector and a DB-225J&W column. The neutral sugars analysis of BX showed the predominance of xylose (97.1%) and the presence of small amounts of