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Hydrophobic films from maize bran hemicelluloses

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Abstract

The covalent binding of laurylamine chains to maize bran heteroxylan (HX) was studied in order to produce hydrophobic plastic films. The process was carried out using periodic oxidation followed by reductive amination, both steps conducted in water. A kinetic study of the first step was performed, measuring periodate consumption, formic acid release and aldehyde formation. The over-oxidation effect was evaluated. The degree of substitution (DS) of dodecylamino-grafted-heteroxylan films ranged between 0.5 and 1.1 and varied as a function of experimental conditions. The maximal DS was reached under the following experimental conditions: $NaIO_4$ 2 eq per sugar unit, laurylamine 1.7 eq, $NaBH_3CN$ 5.8 eq per aldehyde. The plastic behaviour at room temperature was correlated to the glass transition temperature. Mechanical properties in function of the DS and the mode of obtention (casting, tape casting) were evaluated by tensile tests. © 2002 Published by Elsevier Science Ltd.

Keywords: Amination; Bran; Hemicellulose; Heteroxylan; Maize; Oxidation

1. Introduction

The use of lignocellulosic waste material from agricultural crops and forestry as a source of chemicals has received considerable interest in recent years due to their abundance and renewability. These raw materials look promising to replace environmentally unfriendly fossil hydrocarbons and, hence, to create 'green' products.

After cellulose, hemicelluloses constitute the second most abundant class of polysaccharides found in nature. They comprise roughly one-fourth to one-third of most plant materials. During the past twenty years, these by-products have demonstrated a potential fermentation feedstock for the production of sugars (Ohtani, Naoteru, Koyama, Tsutomu, Takeuchi & Takashi, 1997), furfural (Verdeguer, 1990) and found applications as additives in paper-making (El-Ashmawy, Mobarak & El-Kaliobi, 1976), pharmaceutical (Bezanger-Beauquesne, Pinkas, Torck & Trotin, 1991), cosmetic (Whistler & Shah, 1978) and food (Loison, 1991) areas. The obtention of hydrophobic polymers from various hemicelluloses through etherification (Fan & Feng, 1987; Vincendon, 1998) or esterification (Sun, Fang & Tomkinson, 2000; Thiebaud & Borredon, 1998) of hydroxyl groups have received only little attention in comparison to cellulose.

In the present work, we report the obtention of hydrophobic plastic films from maize bran hemicelluloses. Maize bran, an abundant agricultural by-product, is presently of poor added value. Extracted from thick walled cells, this hemicellulose is mainly composed of heteroxylan (HX). This HX consists of a β-1,4-D-xylose backbone highly substituted with short side chains (Chanliaud, Saulnier & Thibault, 1995). Introduction of alkyl chains has been carried out by periodic oxidation followed by reductive amination using water as the unique solvent for all chemical steps. The different steps of this process are presented in Fig. 1.

We have first optimised periodic oxidation and studied the structural modifications induced by this reaction on the HX. Then, an optimisation of the reductive amination process is given and structural features are discussed. Last, we describe some physical behaviours (thermal and mechanical properties) of these new materials.

2. Experimental

2.1. Material

Maize bran and HX have been obtained from

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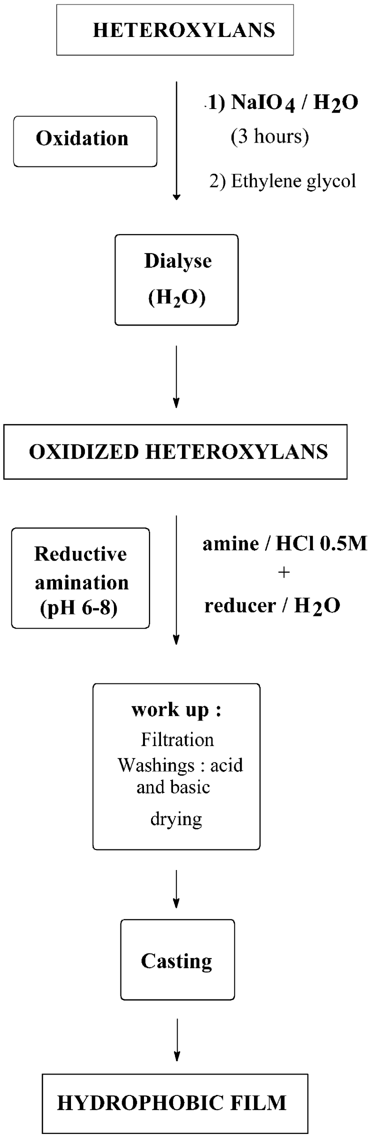


Fig. 1. Process diagram.

ULICE-LIMAGRAIN (63204 Riom, France). Maize bran HX was extracted and purified at pilot scale according to the protocol previously reported by Chanliaud et al. (1980). Extracted HXs exhibited a weight average molecular weight $\bar{M}_w$ of about 2.8×10^5 g mol^{-1}.

Commercially available dodecylamine, sodium cyanoborohydride, sodium and potassium borohydrides and sodium periodate (Aldrich) were used without further purification. Bidistilled water was used throughout this study. Salts and low molecular weight compounds were removed from the medium by dialysis with Spectra/Por regenerated cellulose membranes with a molecular weight cut off (MWCO) of 6000/8000.

2.2. Characterisation of heteroxylans

HX was analysed for neutral sugar composition after hydrolysis of the sample for 2 h at 100°C in 1 M sulphuric acid. Free sugars were reduced to alditols with $NaBH_4$ in 3 M ammonia for 1 h at 40°C. Acetylation of alditols was performed using acetic anhydride in the presence of *N*-Methyl imidazole for 20 min at 20°C. Alditol acetates were extracted with dichloromethane and directly analysed by gas chromatography (GC) on a OV-225 (25 m × 0.32 mm i.d.) fused-silica capillary column (Englyst & Cumming, 1988). Glucuronic acid percentage was estimated by the colorimetric automated *m*-hydroxybiphenyl method (Thibault, 1979).

2.3. Oxidation of heteroxylans

HX (1 g) was first dissolved in 40 ml of water, then added to sodium periodate (2 g) dissolved in 40 ml of water. The reaction mixture was stirred at room temperature for 0.5–20 h in the dark. Excess periodate was reacted with 5 ml ethylene glycol, and the oxidised product was dialysed against distilled water.

Four different initial periodate/α-diol ratios have been used (2, 1, 0.5 and 0.2 equivalents of periodate). The amount of consumed periodate was determined by measuring absorbance at 225 nm. Released formic acid was titrated by sodium hydroxide after adding ethane-1,2-diol to destroy excess periodate (Hay, Lewis & Smith, 1965). A measure of aldehyde mole number was performed using the highest periodate/α-diol ratio (2 eq of periodate), following a method adapted from Pommerening, Rein, Bertram & Müller, 1992): salts and compounds with molecular weight < 6000 were removed by dialysis against distilled water, and an excess of sodium hydroxide was introduced in the medium; after heating at 70°C for one hour, the solution was neutralised by an equivalent amount of hydrochloric acid; then carboxylic functions were titrated with sodium hydroxide.

2.4. Reductive amination of dialdehyde heteroxylan (DAHX)

Dodecylamine was dissolved in 0.5 M HCl under stirring at room temperature and DAHX solution was poured into this mixture. Two different protocols have been designed, depending on the nature of the reducing agent. When $NaBH_4$ (or KBH_4) was chosen, amination was first achieved in a separate step, followed by 24 h reduction. When $NaBH_3CN$ was used as reducing agent, it was introduced at the same time as dodecylamine and pH was adjusted to 6–7; the resulting reaction mixture was stirred at room temperature from 30 min to 4 days. The precipitate was filtered off, washed with acetic acid, saturated solution of sodium hydrogenocarbonate and water.

2.5. Casting and characterisation

The resulting material was dissolved in chloroform and dried on $MgSO_4$. Insoluble particles were removed by

Table 1
Determination of α-diol mole number

Entry Nature of sugar	1 m_s (mg g^{-1})[a]	2 n_s (mmol g^{-1})[b]	3 Position of hydroxyl groups[c]	4 Number of α-diol (A)	5 Molar percentage (B)[d]	6 α-diol (C) (mol g^{-1})[e]
L-araf	227.5	1.72	2,5[c] or 3,5	0	0.38	0
			2,3 or 2,3,5	1	0.62	1.066
D-xylp	370	2.8	2 or 3 or none	0	0.603	0
			2,3	1	0.165	0.462
			2,3,4	2	0.232	1.299
D-galp	58.5	0.36	2,4,6	0	0.058	0
			2,3,4,6 or 2,3,4	2	0.942	0.678
D-glcA	58	0.33	2,3,4,6	2	1	0.66
D-glcp	80	0.49	2,3	1	1	0.49
Summ	794	5.7				4.66

[a] Mass of sugar unit (s) per g of sample.

[b] Mole number of sugar (s) per g of sample.

[c] The positions of non-glycosylated carbons in starting sample are obtained from permethylation analysis(11) (2,5 means that hydroxyl functions are on carbons 2 and 5 of the sugar).

[d] Percentages of monomer giving the same number of α-diol are deduced from permethylation analysis(11).

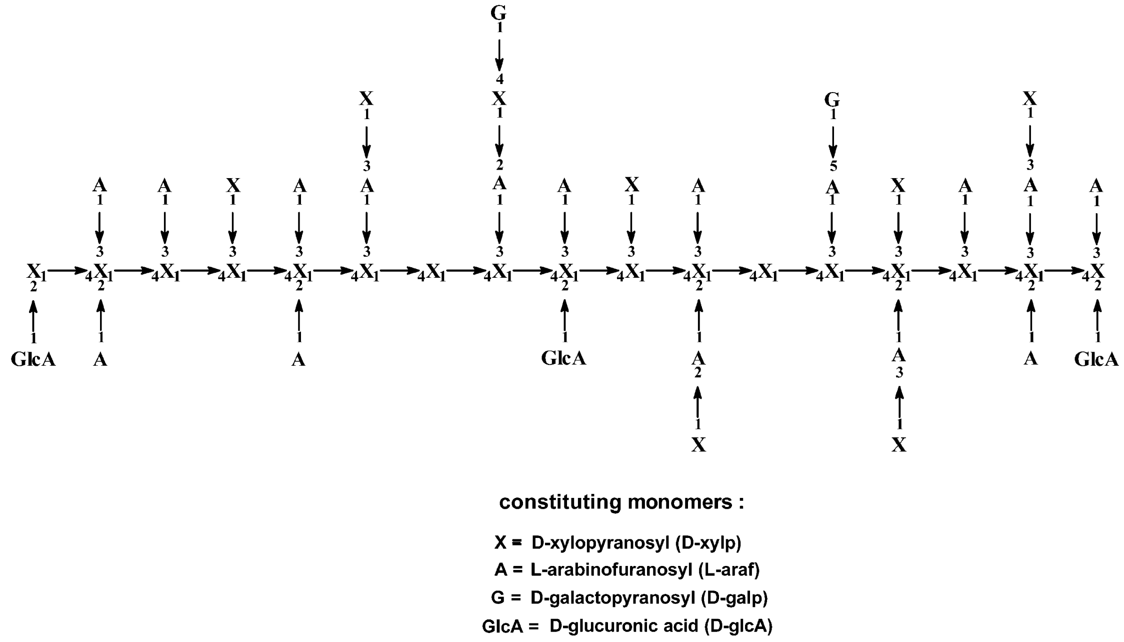
[e] Mole number of α-diol per g of sample, $(C) = n_s(A)(B)$.

filtration. After evaporation (casting), filmogenic properties were first evaluated by visual inspection. The film was further stored under vacuum for 2 days to remove any remaining traces of solvent. FT-IR spectra were recorded on a KBr pellet by transmission or on a ZnSe crystal, by Horizontal Attenuated Total Reflectance, with a FTIR Perkin–Elmer spectrometer. ^{1}H-NMR spectrum of samples was recorded in a 400 MHz Brücker spectrometer. Microanalyses were carried out by the 'Service Régional de Microanalyse de l'Université Pierre et Marie Curie, Paris VI'. Degree of substitution (DS) was determined from carbon percentage using the following formula (1) where (%C) is the carbon percentage, $\bar{M}$m is average molecular mass of a sugar unit, $\bar{M}$c is the average carbon mass of sugar unit, M_{amine} is the molecular mass of amine, $M\text{c}_{\text{amine}}$ is the carbon mass of the amine chain and k equals 1 or 2, depending on the final structure (see Appendix A for details).

$$\text{DS} = \frac{\bar{M}\text{m}(\%\text{C}) - \bar{M}\text{c}}{M\text{c}_{\text{amine}} - (M_{\text{amine}} - k \times M_{\text{OH}})(\%\text{C})} \quad (1)$$

2.6. Thermal analysis

Measurement of calorimetric properties of the materials was performed by differential scanning calorimetry (DSC) on automated DSC 121 equipment (SETARAM, France).



constituting monomers :

X = D-xylopyranosyl (D-xylp)
A = L-arabinofuranosyl (L-araf)
G = D-galactopyranosyl (D-galp)
GlcA = D-glucuronic acid (D-glcA)

Fig. 2. Structure of HXs (from Chanliaud et al., 1980).

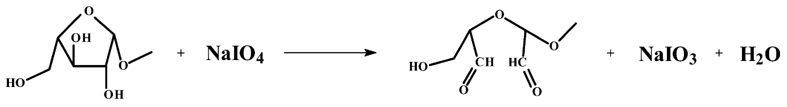


Fig. 3. Periodate oxidation of arabinosyl moiety of HX.

Films were cryogrinded using a cryo-grinder (Spex 6700, Avantec) and placed in pressure-tight DSC cell (about 100 mg of material per cell). A first scanning was performed from −70 to +70°C to erase any thermal events which might have occurred during preparation and storage of the sample. After a rapid cooling (60°C min^{-1}) to −70°C, actual measurement was performed during a second scanning at 3°C min^{-1}.

2.7. Mechanical tests

Films elaborated by casting displaying a DS of 0.7 (A), 1.1 (B), and film elaborated by 'tape-casting' (Mistler, 2000) with a DS of 1.1 (C) were studied. Samples were elaborated with 20.0 ± 0.1 mm width, 0.1 ± 0.01 mm thickness and 31.1 ± 0.1 mm long between the two live loadings. Eight tests were carried out for each film at 19 ± 1°C using a tensile machine. Samples were submitted to vertical deformation at a constant velocity of 500 mm min^{-1}.

3. Results and discussion

3.1. Structural analysis of the heteroxylan starting material

As shown in Table 1, five different sugars were detected: L-arabinofuranose (L-araf) D-xylopyranose (D-xylp), D-galactopyranose (D-galp), D-glucuronic acid (D-glcA) and D-glucopyranose (D-glcp). Mass concentrations m_s (mg per g of sample) were directly obtained from GC analysis. Mass percentages (entry 1) and molar concentration n_s (mmol g^{-1}) were deduced (entry 2). For each sugar, hydroxyl group positions are mentioned (entry 3). Hence, monomers are classified according to their number of α-diol functions (0, 1 or 2). GC analysis of the derived sample showed that molar proportion of arabinose, xylose, galactose and glucuronic acid were in agreement with Chanliaud's results (Fig. 2). Since the sample is not exempted of starch (albumen contamination), glucose residues were also detected (10.0%). We can deduce from these data, that 1 g of HX sample contains about 5.7 mmol of sugars and affords 4.66 mmol of α-diol functions.

3.2. Periodate oxidation of heteroxylan

Periodate oxidation of HX gives an open ring product in which monomers contain two aldehyde functions induced by cleavage of α-diol (Fig. 3). The theoretical amount of sodium periodate necessary to achieve complete oxidation is equal to the mole number of α-diol functions (4.66 mmol g^{-1}). The rate of oxidation was studied in the presence of various periodate/α-diol ratios in order to determine optimal oxidation conditions. Results are plotted in Fig. 4.

When 0.5 or 0.2 equivalents of periodate is used (curves C and D), its consumption quickly reaches (less than 1 h) a constant value. The use of one equivalent of periodate (curve B) does not lead to complete oxidation because the theoretical mole number of consumed periodate (4.66) is not reached. With 2 equivalents of periodate (curve A), the reaction occurs rapidly and becomes very slow after 3 h. We observe otherwise that the theoretical mole number of consumed periodate (4.66) is largely exceeded.

Moreover, di-oxidation of sugars containing α,β-triol functions (xylose, galactose and glucuronic acid units) can also produce formic acid (fa) as shown in Fig. 5. The theoretical amount of formic acid ($n_{\mathrm{fa/di}}^{\mathrm{th}}$) produced from maximum di-oxidation according to Scheme 3 can be calculated from data in Table 1 (n_{xyl}, n_{gal} and n_{glcA} are found in entry 2

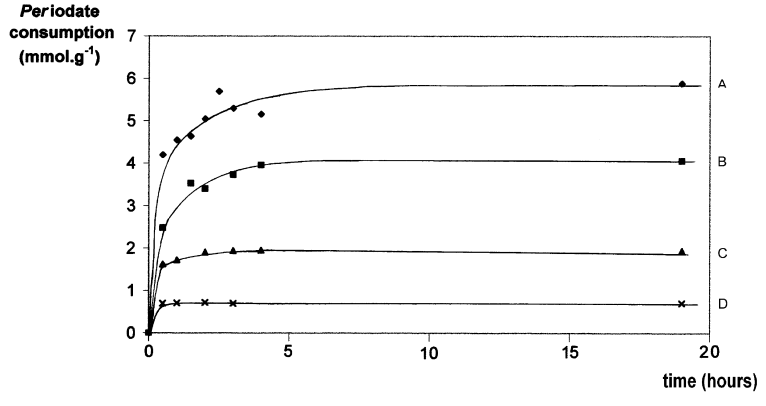


Fig. 4. Consumption of sodium periodate versus time: (A) with 2 equivalents of periodate per α-diol; (B) 1 equivalent; (C) 0.5 equivalent; (D) 0.2 equivalent.

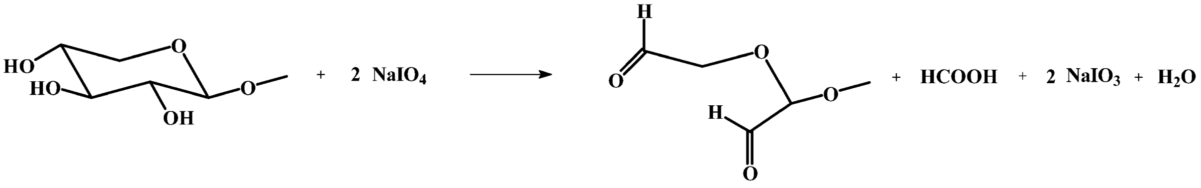


Fig. 5. Periodate di-oxidation of xylosyl moiety of HX.

and percentages in entry 5):

$$(n^{\mathrm{th}}_{\mathrm{fa/di}}) = n_{\mathrm{xyl}} \times 0.232 + n_{\mathrm{gal}} \times 0.942 + n_{\mathrm{glcA}} \times 1 = 1.32\ \mathrm{mmol\ g}^{-1}$$

Formic acid formation was followed in the different initial conditions in order to determine the amount of di-oxidised moieties. Results are plotted in Fig. 6. A comparison between curves A and B and on the other hand, curves C and D points out that high concentrations of periodate lead to continuous formation of formic acid. In curve A, this release continues up to around 20 h, and reaches 2.5 mmol that exceeds the maximum value (1.32 mmol). This indicates that there is an additional source of formic acid production, accompanied by the consumption of periodate (Fig. 4(A)).

The instability of some resulting di-oxidised dialdehyde moieties involves further oxidation, called ‘over-oxidation’. Non reductive glucuronic acid units are subjected to extensive over-oxidation (Cantley, Hough & Pittet, 1963; Perlin, 1980) which leads to the production of formic acid and carbon dioxide as shown in Fig. 7. Over-oxidation is also observed at the reductive end-groups of most of polysaccharides (Cantley et al., 1980). The reaction propagates along the chain, each sugar being degraded one after the other. This phenomenon is increased in linear polysaccharides, but is limited in branched ones. In the case of the strongly branched HX, over-oxidation could be neglected accordingly. In the case of starch, present as a contaminant in the sample, over-oxidation may occur and yield degradation products as shown in Fig. 8.

Thus, over-oxidation can proceed mainly from two sources, glucuronic acid and glucose. In the experiment carried out with 2 equivalents of periodate, it has been shown that more periodate was consumed and more formic acid was released than expected.

Accordingly, formic acid (n_{fa}) is provided in a concomitant manner from both di-oxidation ($n_{\mathrm{fa/di}}$) of xylose and galactose and from over-oxidation ($n_{\mathrm{fa/ov}}$) of glucuronic acid and glucose.

$$n_{\mathrm{fa}} = n_{\mathrm{fa/ov}} + n_{\mathrm{fa/di}} \qquad (2)$$

The relation between mole numbers of produced aldehydes (n_{ald}), consumed periodate (n_{per}) and formic acid released (n_{fa}) and the mole number of formic acid produced only from over-oxidation ($n_{\mathrm{fa/ov}}$) is given by:

$$n_{\mathrm{fa/ov}} = 2(n_{\mathrm{per}} - n_{\mathrm{fa}}) - n_{\mathrm{ald}} \qquad (3)$$

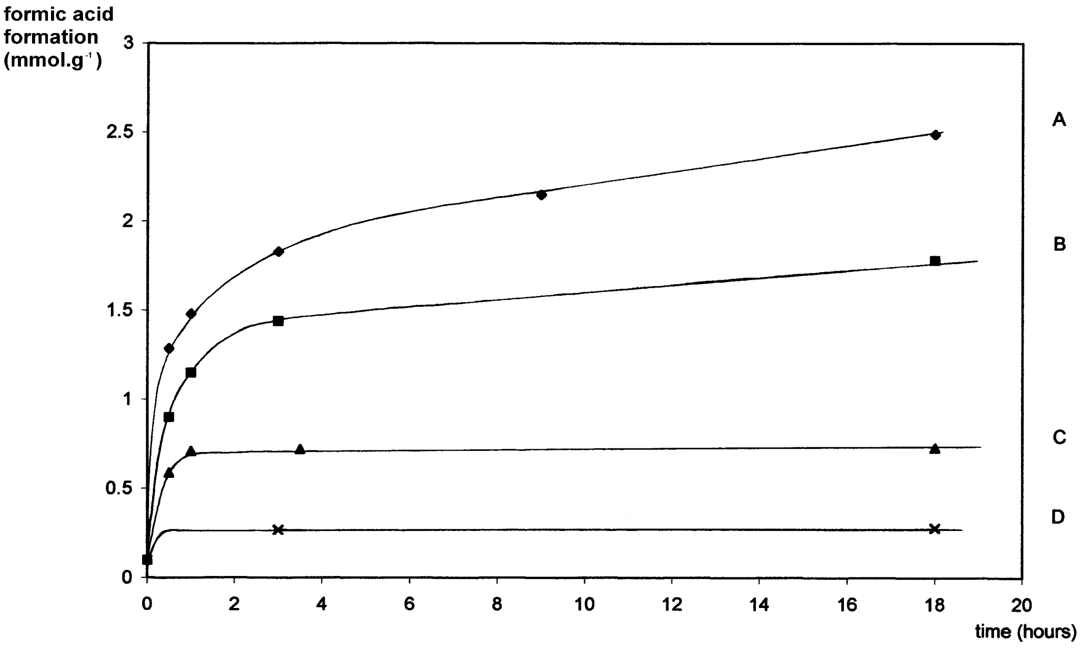


Fig. 6. Formic acid formation versus time: (A) with 2 equivalent of periodate per α-diol; (B) 1 equivalent; (C) 0.5 equivalent; (D) 0.2 equivalent.

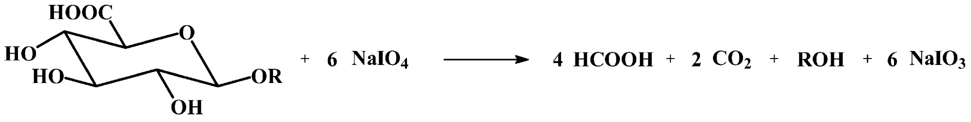


Fig. 7. Periodate over-oxidation of glucuronic acid in HX.

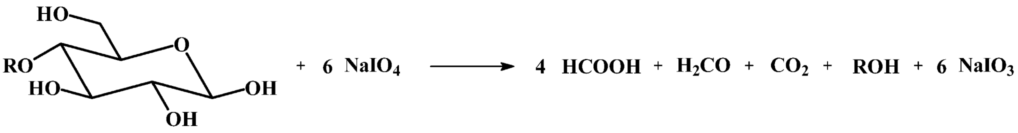


Fig. 8. Periodate over-oxidation of terminal glucose in starch.

Eq. (3) is deduced from Eq. (2) and reactions are described in Figs. 3, 5, 7 and 8. Calculations are given in Appendix B. Then, we deduce the relation giving the mole number of formic acid produced from di-oxidation ($n_{\text{fa/di}}$) from Eqs. (2) and (3):

$$n_{\text{fa/di}} = n_{\text{ald}} - n_{\text{fa}} - 2n_{\text{per}} \tag{4}$$

The mole number of aldehyde functions produced as a function of time was then determined in the case corresponding to maximum oxidised HX (curve A). Results are plotted in Fig. 9. As expected, the amount of aldehyde increases rapidly up to a value of 5.4 mmol g^{-1}.

The knowledge of n_{ald}, n_{per} and n_{af} (Figs. 4, 6 and 9) allows us to determine the mole number of formic acid produced from di-oxidation ($n_{\text{fa/di}}$) and the mole number of formic acid produced from over-oxidation ($n_{\text{fa/ov}}$) as a function of time. Results are plotted in Figs. 10 and 11. It appears from Fig. 10 that the amount of formic acid released by di-oxidation after 3 h reaction time (curve A) reaches 0.15 mmol g^{-1}, whereas the theoretical maximum (B) is 0.99 mmol g^{-1}. This induces the di-oxidation rate (%di) to a value of 15%.

In Fig. 11, the amount of formic acid released by over-oxidation (curve C) rapidly reaches a plateau (1.3 mmol g^{-1}). This plateau corresponds roughly to the amount of formic acid produced by total over-oxidation of glucuronic acid moieties (D). If we assume that over-oxidation of starch occurs significantly, $n_{\text{af/ov}}$ would be higher and would increase to a value ranging between (D) and (E). The determination of maximum limits B, D and E are found in Appendix C. Accordingly, the amount of formic acid released by over-oxidation of starch is negligible. These results strongly support that the over-oxidation rate of glucuronic acid is about 100% after 3 h of reaction.

3.3. Reductive amination of periodate oxidised heteroxylans

Oxidation study has shown that the sample, consisting of a major amount of HX and a minor amount of starch, was fully oxidised and could give 2 aldehyde functions per osidic unity, except uronic ones, which were degraded. At the issue of this step, we did not perform any discrimination between starch and HX. Reductive amination has been conducted on both of them.

3.3.1. Effect of the reducing agent

Several reducers were tested for the reducing step, using dodecylamine as amination agent. The amination of DAHX and subsequent reduction are shown in Fig. 12. Among the different hydrides (Table 2), only sodium cyanoborohydride in acidic medium leads to the formation of a hydrophobic film.

Sodium borohydride has been used by a few authors (Schellenberg, 1963; Wilson & Nakane, 1976) for the reductive step after imine formation. In the present case, the use of this reducer does not lead to plastic material formation. This is certainly due to insufficient substitution of dodecylamine chains, which act here as internal plasticisers. On the contrary, when reductive amination was

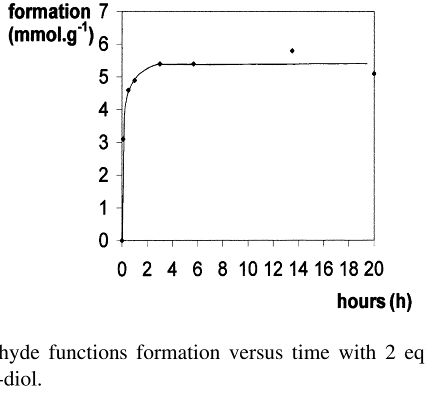


Fig. 9. Aldehyde functions formation versus time with 2 equivalents of NaIO$_4$ per α-diol.

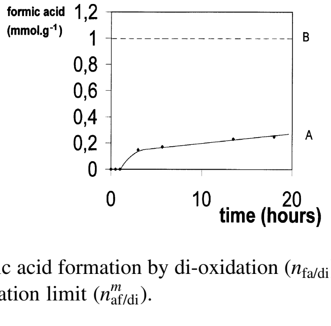


Fig. 10. (A) Formic acid formation by di-oxidation ($n_{\text{fa/di}}$) versus time; (B) maximum di-oxidation limit ($n^{m}_{\text{af/di}}$).

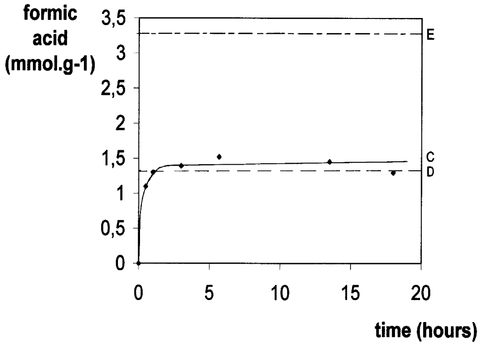


Fig. 11. (C) Formic acid formation by over-oxidation ($n_{\mathrm{af/ov}}$) versus time; (D) total glucuronic acid over-oxidation $(n^{m}_{\mathrm{af/ov}})_{\mathrm{glcA}}$; (E) maximum over-oxidation limit ($n^{m}_{\mathrm{af/ov}}$).

performed with sodium cyanoborohydride in acidic conditions, in one step, we obtained a significant modification of the physical properties of the material, and the apparition of plastic product. The reason lies in the fact that this reducer shifts the amine/iminium equilibrium toward the formation of the iminium species, thanks to rapid and selective attack of hydride on iminium intermediate (Lane, 1975). These conditions lead to more amine fixation than in the case of the two step procedure using borohydride.

3.3.2. DS variations

Therefore, sodium cyanoborohydride was used as a reducer in acidic medium according to Lane's procedure. We have varied the nature and amount of amine and the reaction time (Table 3).

The calculated DS corresponds to the average number of aminated chains covalently bound per monomer unit. Knowledge of the structure of aminated product is necessary for the determination of DS. Two forms, illustrated by an arabinose monomer in Fig. 13, can be expected: either a secondary amine in an open structure 13(1) or a tertiary amine involved in a cyclic structure 13(2). According to Lane, the reaction of a dicarbonyl compound with a primary amine in the presence of sodium cyanoborohydride can provide a cyclic compound. Du and Hindsgaul (1997) by NMR, characterised a cyclic compound obtained from the reaction of a dialdehyde carbohydrate on various amino-acids. Such considerations allow us to expect the occurrence of a cyclic structure 13(2).

In a linear 1 → 4β-xylan, in which the mole number of α-diol-monomers equals the mole number of monomer, reductive amination could lead to a maximum DS of 2 for the open structure 13(1), or 1 for the cyclic one 13(2). Due to the branched structure of HXs, α-diol-sugar mole number is lower than the mole number of monomers. Actually, calculation of $\mathrm{DS}_{\max}$ gives respectively 1.12 (structure 13(1)) and 0.56 (structure 13(2)). Details are given in Appendix D. Experimental DS were calculated using formula 1, with k equal to 1 or 2, depending on whether the structure 13(1) or structure 13(2) is considered (see Appendix A). In the latter case, DS overcomes the upper limit of 0.56 (DS values are found between 0.6 and 0.85). In the former case, results do not exceed the $\mathrm{DS}_{\max}$ (1.12). Moreover, the obtention of a DS value of 1.1 (entry 11, Table 3), rules out the obtention of a cyclic structure for this product. Accordingly, the open structure is generalised to all cases and DS calculations were achieved according to formula (1), with k equal to 1.

We observe a clear correlation between degrees of substitution and appearance of the films. A film is all the more homogeneous as the DS is high, and DS increases with reaction time. There is a noticeable evolution between 30 min and four days of reaction time, but one full day is long enough to obtain a transparent and homogeneous film. The amount of dodecylamine seems to play a non-negligible role on the DS of the product. A slight excess (1.7 equivalent) allows us to obtain an adequate DS, whereas a default or a large excess of amine decreases the DS and gives lower yields.

A reaction time of 24 h with a small excess of dodecylamine and sodium cyanoborohydride efficiently led to

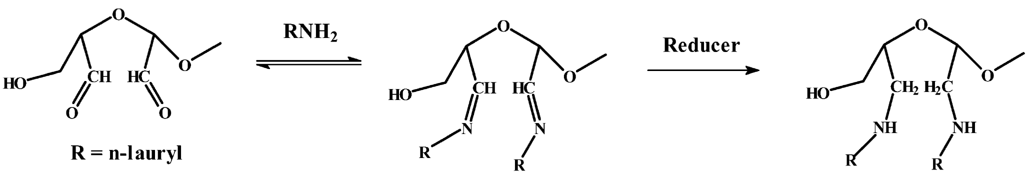


Fig. 12. Reductive amination on a dialdehyde–arabinose moiety of HX.

Table 2
Effect of reducing agent

Reducing agent	Dodecylamine (eq)	Amination time (h)	Sample number	Mass yield[a] (%)	Product aspect
$\mathrm{NaBH_3CN}$, 2.4 g	1.7	24	1	120	Film
$\mathrm{NaBH_4}$, 1.44 g	1.7	24	2	76	Powder
$\mathrm{NaBH_4}$, 1.44 g	3.4	240	3	70	Powder
$\mathrm{KBH_4}$, 2.2 g	1.7	24	4	66	Powder

[a] The mass yield is defined as the ratio of the experimental mass to the starting mass of HX.

Table 3
Reductive amination study

Assay	Reaction time (h)	Dodecylamine (eq)	$NaBH_3CN$ (eq)	Mass yield[a] (%)	DS[b]	Product appearance
1	0.5	1.7	7	100	0.6	Opaque and heterogeneous films
2	4			110	0.6	
3	24			112	0.7	Transparent and homogeneous films
4	48			147	0.9	
5	96			155	0.9	
6	24	0.85	7	50	0.6	Opaque film
7	24	3.4		86	0.5	Brittle film
8	96			100	0.6	Heterogeneous film
9	24	1.7	5.8	130	0.7	Transparent and homogeneous film
10	24		3.5	100	0.8	
11	24		2.4			No conversion
12	96		5.8	155	1.1	Transparent and homogeneous film

[a] The mass yield is defined as the ratio of the experimental mass by initial mass of HX.

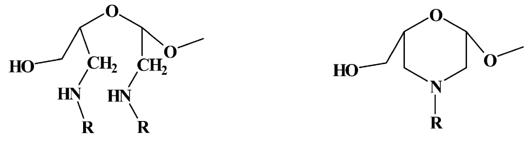
[b] DS are practically calculated based on Eq. (1). See Appendix A for details.

dodecylamino-grafted HXs, with a high mass rate. Using lower amounts of oxidant (underoxidation), lower yields and poorer filmogenic character were obtained (Table 4).

3.3.3. Structural considerations

FT-IR spectra of native and aminated HXs in the frequency range of 680–4000 cm^{-1} are illustrated in Fig. 14. In the starting HX (A), a prominent absorption at 1033 cm^{-1} is attributed to the C–O stretching in hemicelluloses (Kacurakova, Ebringerova, Hirsch & Hromadkova, 1994). A narrow band at 897 cm^{-1} is associated with the β-glycosidic linkages between the sugar units (Gupta, Madan & Bansal, 1987) The absorbance at 1634 cm^{-1} is associated to absorbed water (Kacurakova, Belton, Wilson & Hirsch, 1998). The substitution was confirmed by observing the modifications of the spectrum. The strong absorption at 3200–3400 cm^{-1} (hydroxyl groups) of starting HX decreases significantly due to amine bond formation. The increase in elongation bands at 2850, 2919 (CH_2 stretching) and 2954 cm^{-1} (CH_3 stretching), as well as the deformation band at 1465 cm^{-1} (CH_2 bending) indicate the presence of alkyl chains. The absence of peaks at 3330 and 1485 cm^{-1} is correlated to the fact that the product is free from unreacted starting amine.

Modified HX displays an IR absorption peak at 1564 cm^{-1}, as shown in Fig. 14(B), that could be assigned to N–H deformation. Such a bond provides in theory an elongation band, between 3100 and 3500 cm^{-1}. In practice, a weak peak located close to 3300 cm^{-1} is found. Because of overlap with the wide O–H elongation band, this N–H band is not always visible. Otherwise, a tertiary amine function does not display characteristic signals in IR. Therefore, the close examination of infrared spectrum does reveal the presence of secondary amine (**1**), but cannot not rule out the concomitant formation of tertiary amine (**2**).



(1) (2)

Fig. 13. Possible structures of aminated arabinosyl moieties.

A ^1H NMR spectrum of modified HXs has been recorded (Fig. 15). Substituted alkyl chains give a triplet at 0.9 ppm (CH_3), a strong signal at 1.3 ppm (CH_2). Broad signals above 2.5 ppm can be assigned to carbohydrate protons.

3.3.4. Thermal properties

DSC (Fig. 16) revealed a rather broad endothermic signal which occurred between −30 and 0°C and was assigned to glass transition (T_g). At room temperature, the film is therefore above its glass transition temperature which justifies its plastic character.

3.3.5. Mechanical properties

The mechanical characteristics tested were: (i) the elastic modulus E (MPa) given by the slope of the linear part of

Table 4
Effect of periodate amount

$NaIO_4$ (eq)	Yield (%)	DS	Product appearance
2	112	0.72	Transparent film
1	66	0.34	Opaque film
0.5	68	0.21	No film

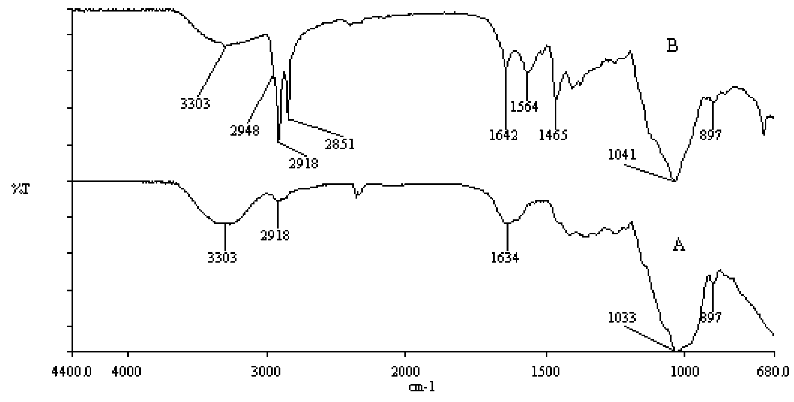


Fig. 14. FT-IR spectra of starting (A) HX and (B) modified HX.

tensile curve (Fig. 17); (ii) the failure tensile stress σ_R (MPa); (iii) the failure axial strain ϵ_R (%).

Mean values are given in Table 5. It can be noticed that the behaviour of the films are clearly affected by the DS and their mode of obtention. The elastic modulus and maximum elongation values are in accordance with the expected ones: an increase of DS leads to a more plastic behaviour (i.e. increase in maximum elongation and decrease in elastic modulus). The tape casting method significantly enhances the plastic character compared to the classical 'casting' method. However, failure tensile stress is not affected by variation of DS or the mode of obtention of films. The failure tensile stress and axial strain parameters of these films are in accordance with some values observed with other plastified carbohydrate biopolymers (Gaudin, Lourdin, Le Botlan, Ilari & Colonna, 1999; Warth, Mülhaupt & Schätzle, 1997).

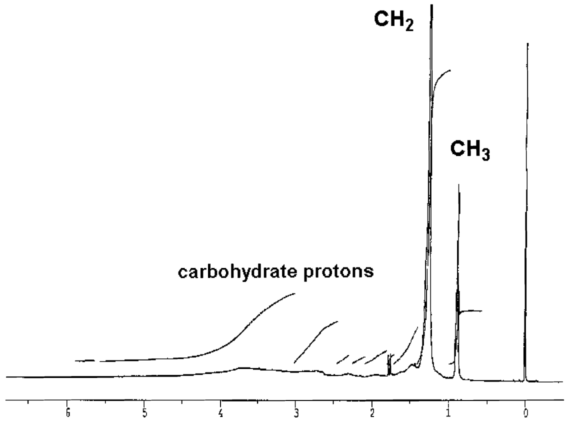


Fig. 15. ^{1}H-NMR spectrum of modified HX.

4. Conclusions

In conclusion, for the first time we have presented the production plastics films from hemicelluloses. The periodic opening of maize bran HX followed by laurylamine linkages with cyanoborohydride, both steps done in water, constitute a suitable and effective method for the preparation of filmogenic plastics. The overall DS can be simply controlled by amination conditions. Under optimal conditions, a product

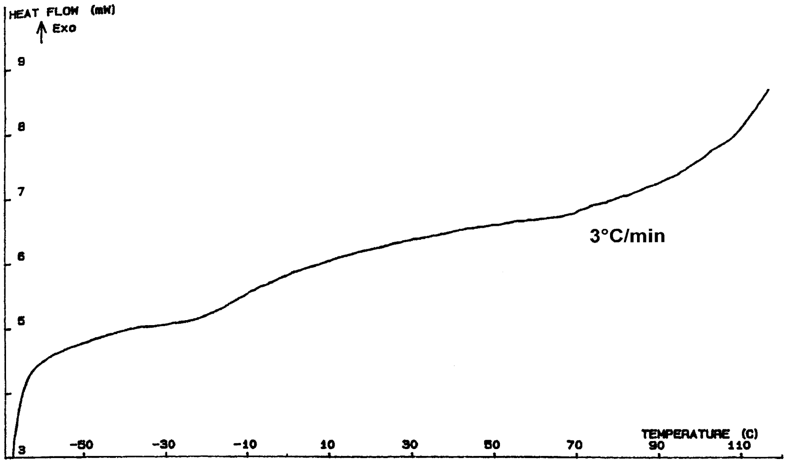


Fig. 16. DSC thermogram of modified HX.

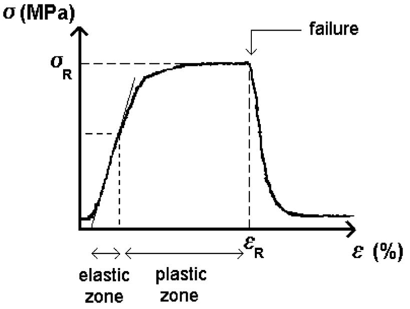


Fig. 17. Tensile stress/strain curve.

with a high DS of 1.1 can be obtained without significant degradation, over-oxidation being nevertheless observed during periodate oxidation in every case. The results obtained from thermal and thermomechanical analyses indicate a glass transition around −30°C, revealing the plastic behaviour of the material at ambient temperature. From a mechanical property point of view, the plastic behaviour is enhanced by high DS. This work opens a new route towards promising applications of hemicelluloses as bio-plastics.

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Appendix A

A.1. DS calculation (formula (1))

This calculation takes into account the percentage of the carbon element in the modified HX

$$\%\mathrm{C} = \frac{\text{Average carbon mass}}{\text{Average total mass}}$$

Each term in this equation can be separated into a saccharidic contribution and an aminated contribution. Owing to the fact that HX is composed of different sugars, each one with a different molar mass, the saccharidic term is an average value. The term related to the aminated part of the equation is a function of DS.

If we privilege an acyclic structure (structure 13(1)), the fixation of an amine results in a loss of 17 g mol^{-1} (O–H), then:

$$\%\mathrm{C} = \frac{\bar{M}\mathrm{c} + M\mathrm{c}_{\mathrm{amine}} \times \mathrm{DS}}{\bar{M}_{\mathrm{m}} - (17 \times \mathrm{DS}) + (M_{\mathrm{amine}} \times \mathrm{DS})}$$

Accordingly,

$$\mathrm{DS} = \frac{\bar{M}_{\mathrm{m}}(\%\mathrm{C}) - \bar{M}_{\mathrm{c}}}{M\mathrm{c}_{\mathrm{amine}} - (M_{\mathrm{amine}} - 17) \times (\%\mathrm{C})}$$

In the hypothesis of a cyclic structure (structure 13(2)), fixation of an amine results in a loss of 34 g mol^{-1} (2 O–H), thus:

$$\%\mathrm{C} = \frac{\bar{M}\mathrm{c} + M\mathrm{c}_{\mathrm{amine}} \times \mathrm{DS}}{\bar{M}_{\mathrm{m}} - (34 \times \mathrm{DS}) + (M_{\mathrm{amine}} \times \mathrm{DS})}$$

Accordingly,

$$\mathrm{DS} = \frac{\bar{M}_{\mathrm{m}}(\%\mathrm{C}) - \bar{M}_{\mathrm{c}}}{M\mathrm{c}_{\mathrm{amine}} - (M_{\mathrm{amine}} - 34) \times (\%\mathrm{C})}$$

A general formula, considering both cases, can be given. The '*k*' factor is introduced and equals to 1 (structure 13(1)) or 2 (structure 13(2)):

$$\mathrm{DS} = \frac{\bar{M}_{\mathrm{m}}(\%\mathrm{C}) - \bar{M}_{\mathrm{c}}}{M\mathrm{c}_{\mathrm{amine}} - (M_{\mathrm{amine}} - k \times M_{\mathrm{OH}}) \times (\%\mathrm{C})} \qquad \text{(A1)}$$

For the calculation of $\bar{M}_{\mathrm{m}}$ and $\bar{M}\mathrm{c}$: osidic molar fraction (X_s) is defined according to:

$$X_s = \frac{n_s}{\sum_s n_s}$$

During periodate oxidation, some of the sugars lose a CHOH group (30 g mol^{-1}) because of di-oxidation. Molar proportion of such sugars are defined in Table 1. The di-oxidation rate (%di) was determined in Section 3.2 and equals 15%. Total carbon masses are 60 for pentoses and 72 for hexoses. Total anhydrosugar masses are 132 for pentoses and 162 for hexoses. Glucuronic acid is not involved in the final structure.

Table 5
Mechanical properties of various films

Film sample	DS	Film obtention method	E (MPa)	σ_{R} (MPa)	ϵ_{R} (%)
A	0.7	Casting	118	10	8
B	1.1	Casting	87	11	22
C	1.1	Tape-casting	57	10	38

Consequently

$$X_{\mathrm{ara}} = 0.32; \qquad X_{\mathrm{xyl}} = 0.52; \qquad X_{\mathrm{gal}} = 0.067;$$

$$X_{\mathrm{glc}} = 0.091,$$

$$\bar{M}_{\mathrm{c}} = (X_{\mathrm{ara}} + X_{\mathrm{xyl}})60 + (X_{\mathrm{gal}} + X_{\mathrm{glc}})72 - (0.232X_{\mathrm{xyl}} + 0.942X_{\mathrm{gal}}) \times \%\mathrm{di} \times 12,$$

$$\bar{M}_{\mathrm{c}} = (0.32 + 0.52)60 + (0.067 + 0.091)72 - (0.232 \times 0.52 + 0.942 \times 0.067)0.15 \times 12,$$

$$\bar{M}_{\mathrm{c}} = 61.4\ \mathrm{g\ mol^{-1}},$$

$$\bar{M}_{\mathrm{m}} = (X_{\mathrm{ara}} + X_{\mathrm{xyl}})132 + (X_{\mathrm{gal}} + X_{\mathrm{glc}})162 - (0.232X_{\mathrm{xyl}} + 0.942X_{\mathrm{gal}}) \times \%\mathrm{di} \times 30,$$

$$\bar{M}_{\mathrm{m}} = (0.32 + 0.52)132 + (0.067 + 0.091)162 - (0.232 \times 0.52 + 0.942 \times 0.067)0.15 \times 30,$$

$$\bar{M}_{\mathrm{m}} = 135.6\ \mathrm{g\ mol^{-1}}$$

Appendix B

B.1. Determination of relation (3)

$$\boldsymbol{n_{\mathrm{fa/di}} = x n_{\mathrm{fa}}} \tag{B1}$$

$$\boldsymbol{n_{\mathrm{fa/ov}} = y n_{\mathrm{fa}}} \tag{B2}$$

with

$$\boldsymbol{x + y = 1} \tag{B3}$$

The mole number of consumed periodate during over-oxidation is, according to Schemes 5 and 6

$$n_{\mathrm{per/ov}} = 6/4 n_{\mathrm{fa/ov}} \tag{B4}$$

The mole number of consumed periodate affording a second cleavage (di-oxidation) is, according to Scheme 4

$$n_{\mathrm{per/di}} = n_{\mathrm{fa/di}} \tag{B5}$$

The mole number of consumed periodate without leading to further aldehyde formation is:

$$n'_{\mathrm{per}} = n_{\mathrm{per/ov}} + n_{\mathrm{per/di}} \tag{B6}$$

From Eqs. (B4), (B5) and (B6), we obtain:

$$n'_{\mathrm{per}} = 6/4 n_{\mathrm{fa/ov}} + n_{\mathrm{fa/di}} \tag{B7}$$

According to Eqs. (B1) and (B2)

$$n'_{\mathrm{per}} = 3/2 y n_{\mathrm{fa}} + x n_{\mathrm{fa}} \tag{B8}$$

and from Eq. (B3)

$$n'_{\mathrm{per}} = 3/2 y n_{\mathrm{fa}} + (1 - y) n_{\mathrm{fa}} \tag{B9}$$

n_{per} is the total mole number of consumed periodate. The mole number n''_{per} of consumed periodate giving two aldehydic groups, according to classical reaction of α-diols (Scheme 2) is:

$$n''_{\mathrm{per}} = n_{\mathrm{per}} - n'_{\mathrm{per}}$$

from Eq. (B9), we obtain

$$n''_{\mathrm{per}} = n_{\mathrm{per}} - n_{\mathrm{fa}}(1/2y + 1)$$

Consequently, the mole number of formed aldehydes is $2 \times n''_{\mathrm{per}}$, that is to say

$$n_{\mathrm{ald}} = 2n_{\mathrm{per}} - (2 + y)n_{\mathrm{fa}}$$

by deduction, relation (3) is given as:

$$n_{\mathrm{fa/ov}} = 2(n_{\mathrm{per}} - n_{\mathrm{fa}}) - n_{\mathrm{ald}}$$

Appendix C

Determination $(n^{m}_{\mathrm{af/di}})$, $(n^{m}_{\mathrm{af/ov}})_{\mathrm{glcA}}$ and $(n^{m}_{\mathrm{af/ov}})$. These values are illustrated in Figs. 10 and 11 through B, D and E plots, respectively.

In the following calculation, molar percentages of sugars comprising α,β-triols (i.e. 0.232 and 0.942) are obtained from Table 1, entry 5.

$$(n^{m}_{\mathrm{af/di}}) = n_{\mathrm{xyl}}0.232 + n_{\mathrm{gal}}0.942 = 0.65 + 0.34 = 0.99\ \mathrm{mmol\ g^{-1}}\ \text{(plot B)},$$

$$(n^{m}_{\mathrm{af/ov}})_{\mathrm{glcA}} = 4n_{\mathrm{glcA}} = 0.33 \times 4 = 1.32\ \mathrm{mmol\ g^{-1}}\ \text{(plot D)},$$

$$(n^{m}_{\mathrm{af/ov}})_{\mathrm{glc}} = 4n_{\mathrm{glc}} = 0.49 \times 4 = 1.96\ \mathrm{mmol\ g^{-1}},$$

$$(n^{m}_{\mathrm{af/ov}}) = 1.32 + 1.96 = 3.38\ \mathrm{mmol\ g^{-1}}\ \text{(plot E)}$$

Appendix D

Determination of theoretical maximum DS following the structure obtained

$$\mathrm{DS}_{1\max} = \frac{2\sum_{s} n_{s,\alpha\text{-diol}}}{\sum_{s} n_{s}}\ \text{(opened structure 1)},$$

$$\mathrm{DS}_{2\max} = \frac{1\sum_{s} n_{s,\alpha\text{-diol}}}{\sum_{s} n_{s}}\ \text{(cyclic structure 2)}$$

$$\sum_{s} n_{s} = n_{\mathrm{ara}} + n_{\mathrm{xyl}} + n_{\mathrm{gal}} + n_{\mathrm{glc}} = 1.72 + 2.8 + 0.36 + 0.49 = 5.37\ \mathrm{mmol},$$

$$\sum_{s} n_{s,\alpha\text{-diol}} = 62\%n_{\mathrm{ara}} + 39.7\%n_{\mathrm{xyl}} + 94.2\%n_{\mathrm{gal}} + n_{\mathrm{glc}},$$

$$\sum_{s} n_{s,\alpha\text{-diol}} = 0.62n_{\mathrm{ara}} + 0.397n_{\mathrm{xyl}} + 0.942n_{\mathrm{gal}} + n_{\mathrm{glc}},$$

$$\sum_{s} n_{s,\alpha\text{-diol}} = 1.066 + 1.11 + 0.339 + 0.49 = 3\ \mathrm{mmol}$$

we can deduce

$$DS_{1\max} = 1.12, \qquad DS_{2\max} = 0.58$$

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