



## Acetylation and characterization of xylan from hardwood kraft pulp

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### ABSTRACT

Alkaline treatment of eucalyptus hardwood kraft pulp with 10% NaOH yielded 6–8% xylan. The acetylation of the extracted xylan was carried in DMAC/LiCl/pyridine system to obtain a series of xylan acetates with different degrees of substitution (DS). Structure elucidation of xylan and xylan acetate was obtained by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy and other homonuclear and heteronuclear 2D-NMR techniques. Inverse-gated <sup>13</sup>C NMR was employed to determine the DS of xylan acetate. Furthermore, results also revealed equal reactivities at the C-2 and C-3 positions of xylan towards acetylation. Thermal stability, solubility behavior and nanofiber formation of xylan acetate were influenced by its DS values. The mechanical properties of xylan acetate propionate were also investigated.

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### 1. Introduction

Renewable materials have been the subject of much research with the aim to replace non-biodegradable petroleum-based polymers. Numerous studies have exploited the use of plant polysaccharides (e.g. cellulose and starch) as substrates for chemical modification. These products were used to develop plastics, films and nanofibers (Amim, Kosaka, Petri, Maia, & Miranda, 2009; Son, Youk, & Park, 2006; Yang & Montgomery, 2008). In addition, they were also considered suitable for agricultural (e.g. controlled release of fertilizers) and medical applications (e.g. hemodialysis and blood filtration) (Aburto et al., 1999).

Aside from cellulose and starch, hemicelluloses also represent one of the most abundant renewable polysaccharides found in nature. They belong to the second largest class of lignocellulosic materials which comprise about one-fourth to one-third of the plant's material (Fang, Sun, Fowler, Tomkinson, & Hill, 1999). The predominating polysaccharide belonging to this class is xylan. It consists of D-xylp (D-xylopyranose) units in the backbone linked by β-(1 → 4) glycosidic bonds. Depending on the source, naturally occurring xylan is usually substituted with sugar units and O-acetyl groups. Homoxylans can be isolated from higher plants such as guar seed husk (Ebringerova & Heinze, 2000). On the other hand, xylan obtained from seaweeds (*Palmariales* sp. and *Bryopsis* sp.) has a backbone of D-xylp residues linked by β-(1 → 3) or mixed β-(1 → 3) and β-(1 → 4) (Heinze, 2005).

Xylan can be easily extracted by alkaline treatment with KOH, NaOH or DMSO (Janzon, Saake, & Puls, 2008). On a dry weight basis, xylan comprises 10–15% in softwoods, 10–35% in hardwoods and up to 40% of agricultural residues in annual plants (Hettrich et al., 2006). O-Acetyl-4-O-methyl glucuronoxylan and arabinosyl-4-O-methylglucuronoxylan are the main hemicelluloses found in hardwood and in softwood, respectively (Cacais, Silveira, & Ferreira, 2001). Hardwood xylan has 4-O-methylglucuronic acid (MeGlcA) residues attached to the C-2 position of the D-xylp residues in the main chain. Approximately 10% of the D-xylp residues in hardwood xylan have this substitution. In addition, 70% of the D-xylp residues in hardwood xylan is acetylated at the C-2 and/or C-3 positions. In contrast, for softwood xylan, 20% of the D-xylp residues are branched with MeGlcA and 13% are branched with α-L-arabinofuranose at the C-3 position (Coughlan & Hazlewood, 1993). Unlike hardwood xylan, softwood xylan is not acetylated. The degree of polymerization of xylan varies depending on the wood species from 150 to 200 in hardwoods and 70 to 130 in softwoods (Saha, 2003). The structure of xylan in annual plants is more complex due to the presence of arabinofuranose, xylopyranose, rhamnose, glucuronic acid and acetyl groups attached to the main chain (Hettrich & Fanter, 2010).

Despite xylan's abundance in nature, cellulose and starch are more commonly used as raw materials for derivatization due to xylan's inherent low molecular weight and heterogeneous structure. Recently, xylan is gaining importance for the basis of new biopolymeric materials and functional biopolymers by chemical modification. Various studies on the esterification of arabinoxylan with different acyl compounds in homogeneous system had already been explored (Fang, Sun, Tomkinson, & Fowler, 2000; Peng et al.,

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2008; Ren, Sun, Liu, Cao, & Luo, 2007; Sun, Fang, Tomkinson, & Jones, 1999; Sun, Sun, & Sun, 2004). The resulting derivatives offer potential applications for the production of biodegradable plastics, resins and films. Several reports have also been made on the film forming properties of xylan and its blends (Buchanan et al., 2003; Gabriell, Gatenholm, Glasser, Jain, & Kenne, 2000; Goksu, Karamanlioglu, Bakir, Yilmaz, & Yilmazer, 2007; Kayserilioglu, Bakir, Yilmaz, & Akkas, 2003; Shaikh, Pandare, Nair, & Varma, 2009).

In this study, xylan from hardwood kraft pulp was isolated by NaOH extraction. Structure elucidation of the xylan based on NMR spectroscopy is discussed in this paper. This work also presents the acetylation of the extracted xylan by homogeneous reaction in DMAc/LiCl/pyridine system. Characterization of xylan acetate in terms of degree of substitution (DS) and its structural features are considered to be one of the important highlights of this research. Thermal properties, solubility behavior and nanofiber formation of xylan acetate were also investigated. In addition, the mechanical properties of xylan acetate propionate films with different DS were discussed as well.

## 2. Materials and methods

### 2.1. Materials

Bleached hardwood kraft pulp sheets from Eucalyptus were donated by the Pulp and Paper Laboratory, The University of Tokyo, Tokyo, Japan. *N,N*-dimethylacetamide (DMAc), lithium chloride (LiCl) and other reagents were purchased from Wako Chemicals.

### 2.2. Extraction of hardwood xylan

Hardwood kraft pulp sheets were cut into pieces and placed in a blender with deionized water. The mixture was blended for 30 s and filtered. The resulting pulp was then mixed with 10% NaOH (1:20) at room temperature. After 2 h, the mixture was filtered and the filtrate was neutralized with acetic acid. Ethanol was added to the mixture until twice the original volume. The mixture was allowed to stand overnight and the precipitate was collected by centrifugation and washed three times with distilled water.

### 2.3. Synthesis of xylan acetate

Previously dried xylan (100 mg) and DMAc (2 ml) were placed in a flask equipped with a condenser. The mixture was heated at 120 °C for 2 h with stirring. After cooling to 100 °C, LiCl (0.175 mg) was added. Stirring was continued at room temperature until all the xylan has dissolved into the solution (ca. 5 h), after which, pyridine (0.24 ml) and acetic anhydride (0.28 ml) were added to the mixture and stirred for 0.5, 1, 2, 3, 4 and 6 h at 50 °C. At the end of the reaction, the mixture was poured slowly in excess ethanol and filtered. The precipitate was dissolved in a small amount of chloroform and reprecipitated with ethanol three times. The resulting xylan acetate was dried *in vacuo* for 12 h at room temperature.

### 2.4. Nuclear magnetic resonance (NMR) analysis

<sup>1</sup>H, <sup>13</sup>C, DQF-COSY (double quantum-filtered correlation spectroscopy), and HSQC (heteronuclear single-quantum correlation) NMR spectra were obtained from a JEOL spectrophotometer operating at 500 MHz. The spectra were recorded at 25 °C. Chemical shifts ( $\delta$  in ppm) were expressed relative to the resonance of Me<sub>4</sub>Si (TMS;  $\delta$  = 0). Samples for NMR analysis were prepared by dissolving 20 mg xylan in 1 ml DMSO-*d*<sub>6</sub>. In the case of xylan acetate, CDCl<sub>3</sub> was used as solvent.

### 2.5. Determination of degree of substitution (DS)

#### 2.5.1. Perpropionylation of xylan acetate

Fifty milligrams of xylan acetate were mixed in a solution of pyridine (1 ml) and propionic anhydride (0.4 ml) for 16 h at 50 °C. The mixture was poured slowly in excess ethanol with stirring and followed by filtration. Reprecipitation was done three times and dried as mentioned in Section 2.3.

#### 2.5.2. DS analysis

Perpropionylated samples dissolved in CDCl<sub>3</sub> (20 mg/ml) were analyzed by <sup>13</sup>C NMR spectroscopy using inverse-gated technique. The degree of substitution was calculated based on the area of the carbonyl peaks of acetyl and propionyl groups. Peaks were assigned by HMBC (heteronuclear multiple bond correlation) NMR spectroscopy.

### 2.6. Solubility behavior

Twenty milligrams of xylan acetate was dissolved in 1 ml CHCl<sub>3</sub> at room temperature. The undissolved solids were separated by centrifugation and dried. The percentage solubility was calculated based on the weight difference divided by the original weight.

### 2.7. Thermogravimetric analysis (TGA)

The thermal stability of xylan, xylan acetate and xylan acetate propionate was observed using a Rigaku Thermoplus TG-8120. Approximately 1 mg of sample was placed in an aluminum pan and heated from 50 to 450 °C at 20 °C/min. Nitrogen was used as the purge gas.

### 2.8. Electrospinning

A dope solution was prepared by dissolving xylan acetate in 1,1,1,3,3,3-hexafluoro-2-propanol to a final concentration of 10 wt./vol.-%. Nanofibers were made using an Esprayer ES-2000 electrospinning device (Fuence, Co. Ltd.). The dope solution (0.5 ml) was drawn into a 1 ml syringe with a needle diameter of 0.5 mm. The voltage applied to the needle was 30 kV and the dope solution was extruded at a speed of 1.4 ml h<sup>-1</sup>. Nanofibers were collected on an aluminum substrate perpendicular to and 15 cm from the needle and dried *in vacuo* overnight.

### 2.9. Scanning electron microscopy

Nanofiber mats were transferred on a SEM stud and coated with platinum. The images were captured using a Hitachi S-4000 SEM at 7 kV.

### 2.10. Preparation of xylan acetate propionate films

Films were prepared by solvent casting method at room temperature. Two hundred milligrams (200 mg) of xylan propionate were dissolved in 10 ml chloroform. The solution was poured into a teflon dish and covered with aluminum foil with tiny holes to allow slow evaporation. The samples were dried *in vacuo* overnight prior to mechanical testing.

### 2.11. Mechanical characterization

The mechanical properties of xylan ester films (20 mm × 1.5 mm) were carried out at room temperature using a Shimadzu EZ test with a load cell of 10 N. A crosshead speed

of 20 mm/min and a 10 mm distance between grips were the parameters used. Five replicates were tested on each sample.

### 3. Results and discussion

#### 3.1. Extraction of xylan

The presence of significant amount of xylan and minor lignin impurities makes hardwood paper grade pulp a good raw material for the extraction of xylan. Solvents known to extract xylan include DMSO, NaOH and KOH (Janzon et al., 2008). In this current research, 10% NaOH was used to extract xylan from hardwood kraft pulp and the yield was 6–8%. Higher alkaline concentration was also employed. Although it produced higher yield, the xylan obtained had lower  $M_w$  (data not shown).

In this study, different NMR experiments were conducted to elucidate the complete structure of the isolated xylan in DMSO- $d_6$ . The  $^1\text{H}$  NMR spectrum of xylan is presented in Fig. 1a. The  $\beta$ -(1  $\rightarrow$  4)-linked D-xylp units were characterized by the signals at  $\delta$  3.0, 3.2, 3.3, 3.5, 3.9 and 4.3 ppm, which correspond to H-2, H-5<sub>a</sub>, H-3, H-4, H-5<sub>e</sub> and H-1, respectively. The DQF-COSY spectrum displayed in Fig. 1b confirms the assignment. Furthermore, it is noted that the two signals which are found downfield at  $\delta$  5.1 and 5.2 ppm show a weak correlation with H-3 and H-2, respectively. These signals originated from the protons of the hydroxyl groups attached at C-3 (–C–OH,  $\delta$  5.1 ppm) and C-2 (–C–OH,  $\delta$  5.2 ppm) positions of the D-xylp units in xylan.

Fig. 1c shows the  $^{13}\text{C}$  NMR spectrum. The five major signals at  $\delta$  63.3, 72.7, 74.0, 75.5 and 101.8 ppm are assigned to C-5, C-2, C-3, C-4 and C-1 of the D-xylp units in xylan. No other additional signals were observed indicating that the isolated xylan does not contain any acetyl groups, 4-O-methylglucuronic acid (MeGlcA), neutral sugars and lignin. According to literature (Teleman, Tenkanen, Jacobs, & Dahlman, 2002), acetyl groups are cleaved from its main chain during alkaline extraction. Likewise, the MeGlcA, neutral sugars and lignin may have also been removed either during the pulping or extraction process. Thus, based on the above observations the isolated hemicellulose was a homoxylan.

#### 3.2. Characterization of xylan acetate

Synthesis of xylan acetate was carried out by homogeneous reaction in DMAC/LiCl/pyridine system at 50 °C. The structural features of xylan acetate were analyzed by employing different NMR experiments. A  $^1\text{H}$  NMR spectrum of a fully acetylated xylan (DS = 2.0) is presented in Fig. 2a. The signals within the range of  $\delta$  3.3–5.0 ppm are assigned to the ring protons of xylan acetate. The strong signal at  $\delta$  2.0 ppm arising from the methyl protons (–CH<sub>3</sub>) confirms the successful acetylation of xylan. Fig. 2b presents the DQF-COSY spectrum showing the correlation between the ring protons of xylan acetate. Based on the spectrum, the signals at  $\delta$  3.3, 3.7, 3.9, 4.5, 4.7 and 5.0 ppm are assigned to H-5<sub>a</sub>, H-4, H-5<sub>e</sub>, H-1, H-2 and H-3 of xylan acetate. The weak cross peak, which is seen at  $\delta\text{H}_x/\delta\text{H}_y = 3.9/3.7$  indicates the correlation between the H-5 at the equatorial position and the H-4 at the axial position. A more distinct cross peak is observed at  $\delta\text{H}_x/\delta\text{H}_y = 3.3/3.7$  showing the correlation between the H-5 at the axial position and the H-4 at the axial position. Hence, the signals at  $\delta$  3.3 and 3.9 ppm are assigned to H-5<sub>a</sub> and H-5<sub>e</sub>, respectively.

The  $^{13}\text{C}$  NMR spectrum of xylan acetate is presented in Fig. 2c. The signal at 20.8 ppm originates from the methyl carbons. This further supports the data indicating the acetylation of xylan. The signals at  $\delta$  62.4, 70.8, 71.8, 74.5 and 100.1 ppm are assigned to C-5, C-2, C-3, C-4 and C-1 of xylan acetate. The

assignment of the ring carbons was done by HSQC NMR analysis which showed the correlation of the ring protons and ring carbons (data not shown). Furthermore, the signals at  $\delta$  169.3 and 169.8 ppm correspond to the carbonyl carbons at the C-3 and C-2 positions, respectively. The assignment of the signals was based on the data obtained from the HMBC NMR analysis which will be discussed later in this section. The absence of other signals indicates that the xylan acetate was free of any unreacted reagents.

Each xylose unit in xylan has two hydroxyl groups available for acetylation. In order to monitor the DS, a series of xylan acetate was synthesized at varying reaction times. At 3 h reaction time, 50% of the hydroxyl groups of xylan was acetylated (DS = 1.1). Complete acetylation of xylan (DS = 2.0) was achieved within 6 h reaction time as shown in Table 1.

The DS of xylan acetate was investigated after perpropionylation of partially substituted xylan acetate followed by inverse-gated  $^{13}\text{C}$ -NMR analysis. During perpropionylation, any unreacted hydroxyl groups present in xylan acetate were esterified with propionic anhydride. Based on the  $^{13}\text{C}$ -NMR spectrum (Fig. 3), the signals found at  $\delta$  9.1 and 27.5 ppm are assigned to the methyl (–CH<sub>3</sub>) and methylene (–CH<sub>2</sub>–) protons of the propionyl groups. In addition, the carbonyl carbons of acetyl and propionyl groups are seen at different chemical shifts. Based on the HMBC spectrum shown in Fig. 3, the carbonyl carbon signals of the acetyl group at the C-2 and C-3 positions occurred at  $\delta$  169.4 and 169.9 ppm, respectively. The carbonyl carbon signals of the propionyl group at the C-2 and C-3 positions are seen at  $\delta$  172.8 and 173.3 ppm, respectively.

The DS of xylan acetate was calculated based on the integral of the carbonyl carbon peaks. Such method calculates not only for the total DS but also for the partial DS at the C-2 and C-3 positions of xylan acetate. The DS values are calculated applying Eqs. (1) and (2):

$$\text{DS}_{\text{Ac}} \text{ at C-2} = \frac{I_A}{I_A + I_B + I_C + I_D} \times 2 \quad (1)$$

$$\text{DS}_{\text{Ac}} \text{ at C-3} = \frac{I_B}{I_A + I_B + I_C + I_D} \times 2 \quad (2)$$

I: integral; A: C=O<sub>Ac</sub> at C-2; B: C=O<sub>Ac</sub> at C-3; C: C=O<sub>Pr</sub> at C-2; D: C=O<sub>Pr</sub> at C-3.

Aside from the DS, the same method is used to determine the regioselectivity of the acetylation reaction. Table 1 summarizes the results of acetyl distribution for xylan acetate synthesized at different reaction times. Data show that the DS values at the C-2 and C-3 positions of xylan acetate are almost the same. This implies that the hydroxyl groups at the C-2 and C-3 positions of xylan towards acetylation reaction have equal reactivities.

#### 3.3. Thermogravimetric analysis (TGA)

One of the factors that affect the thermal properties of a polymer is its composition. The chemical modification of a polymer leads to a change in its thermal stability. Fig. 4a shows a comparison of the thermal properties of xylan and xylan acetate with different DS. The sudden drop in the curve of xylan during the early stage of heating is due to the water loss of the sample. At 50% weight loss, the decomposition temperature of xylan was at 297 °C. In the case of xylan acetate with a DS of 0.6, 1.1, 1.6 and 2.0, the decomposition temperatures were at 294, 312, 348 and 355 °C, respectively. The high thermal stability of xylan acetate is brought about by the decrease in the number of remaining hydroxyl groups after acetylation (Aburto et al., 1999). These hydroxyl groups are oxidized during heating.

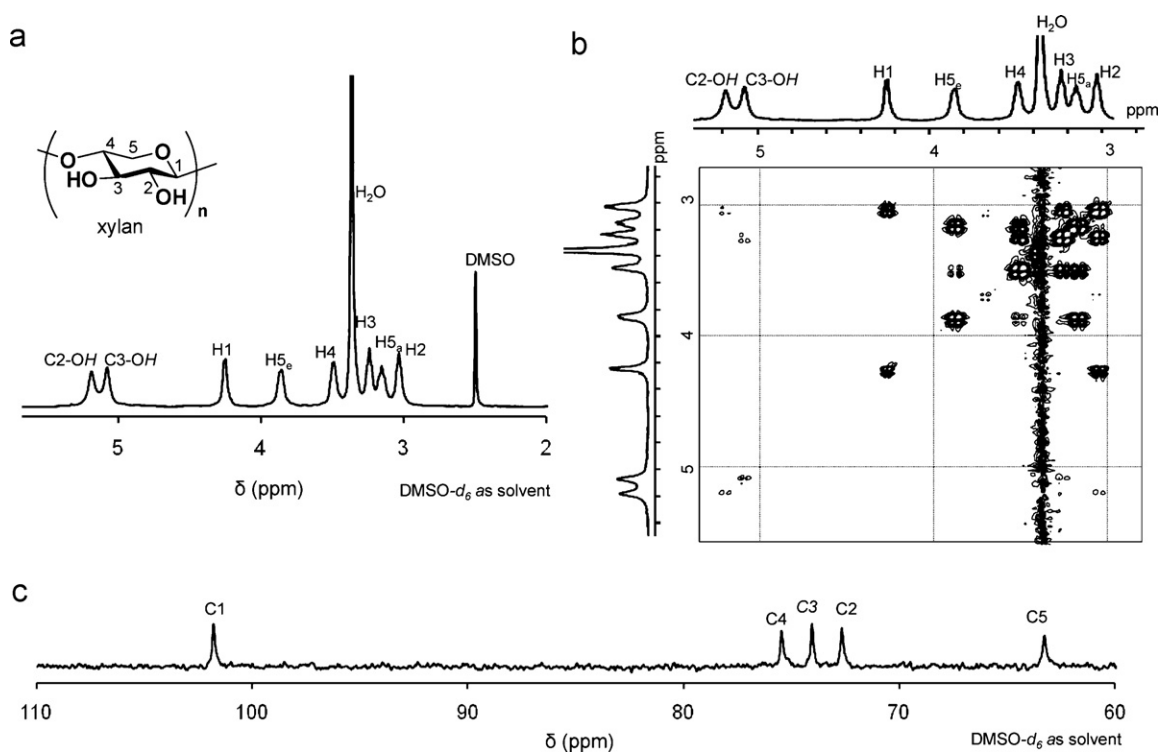


Fig. 1.  $^1\text{H}$  (a) and DQF-COSY (b) and  $^{13}\text{C}$  (c) NMR spectra of xylan extracted from hardwood kraft pulp with 10% NaOH.

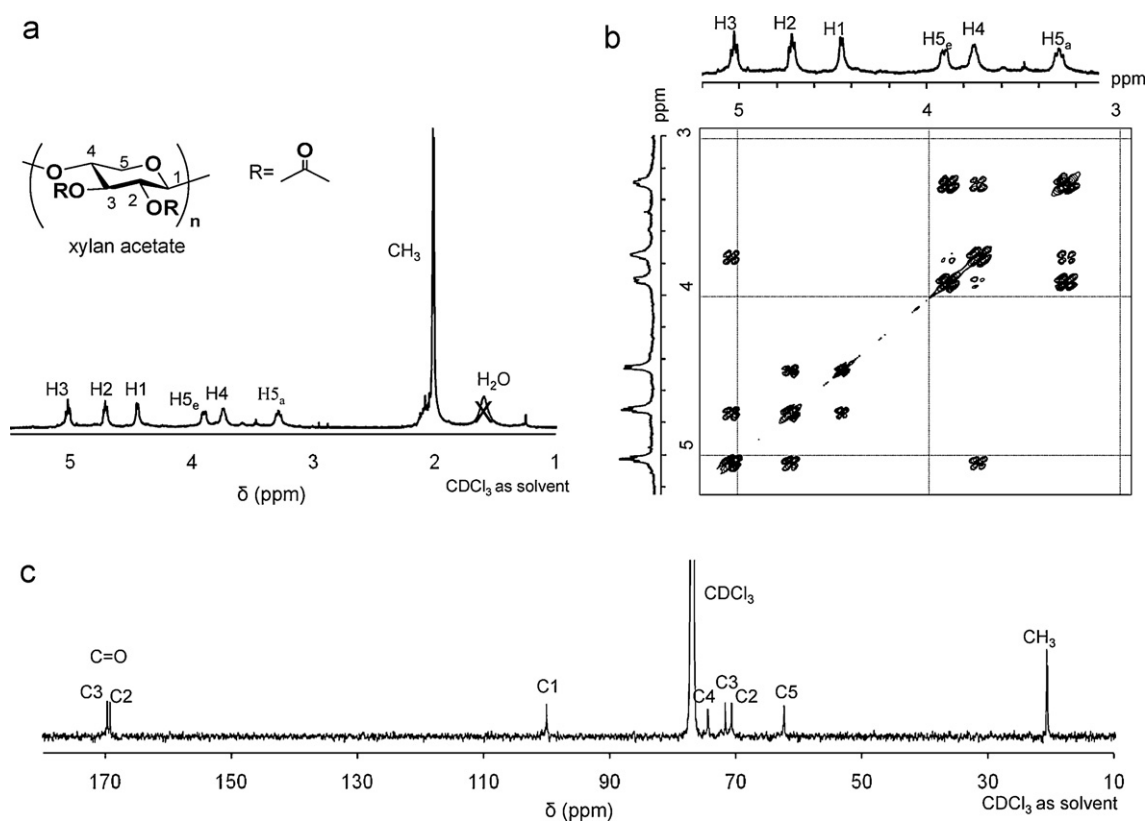


Fig. 2.  $^1\text{H}$  (a) and DQF-COSY (showing the region of the ring protons) (b) and  $^{13}\text{C}$  (c) NMR spectra of xylan acetate (DS=2.0).

**Table 1**  
DS of xylan acetate obtained at different reaction times.

Time (h)	Integral				DS <sub>Ac</sub>			DS <sub>Pr</sub>
	C=O <sub>Ac</sub>		C=O <sub>Pr</sub>		C2	C3	Total	
	C2	C3	C2	C3				
0.5	0.77	0.51	1.19	1.89	0.4	0.2	0.6	1.4
1	0.39	0.34	0.94	1.00	0.3	0.3	0.6	1.4
2	1.00	0.81	0.74	0.86	0.6	0.5	1.1	0.9
3	1.26	1.53	0.29	0.40	0.7	0.9	1.6	0.4
6	0.60	0.60	–	–	1.0	1.0	2.0	0

Fig. 4b compares the TG curves of xylan acetate (DS = 1.1) and xylan acetate propionate (DS<sub>Ac</sub> = 1.1). At 50% weight loss, the decomposition temperatures of xylan acetate and xylan acetate propionate occurred at 312 and 373 °C, respectively. These results indicate that the perpropionylation of partially substituted xylan acetate leads to an increase in its thermal stability. The same results were also observed with the other samples of different DS.

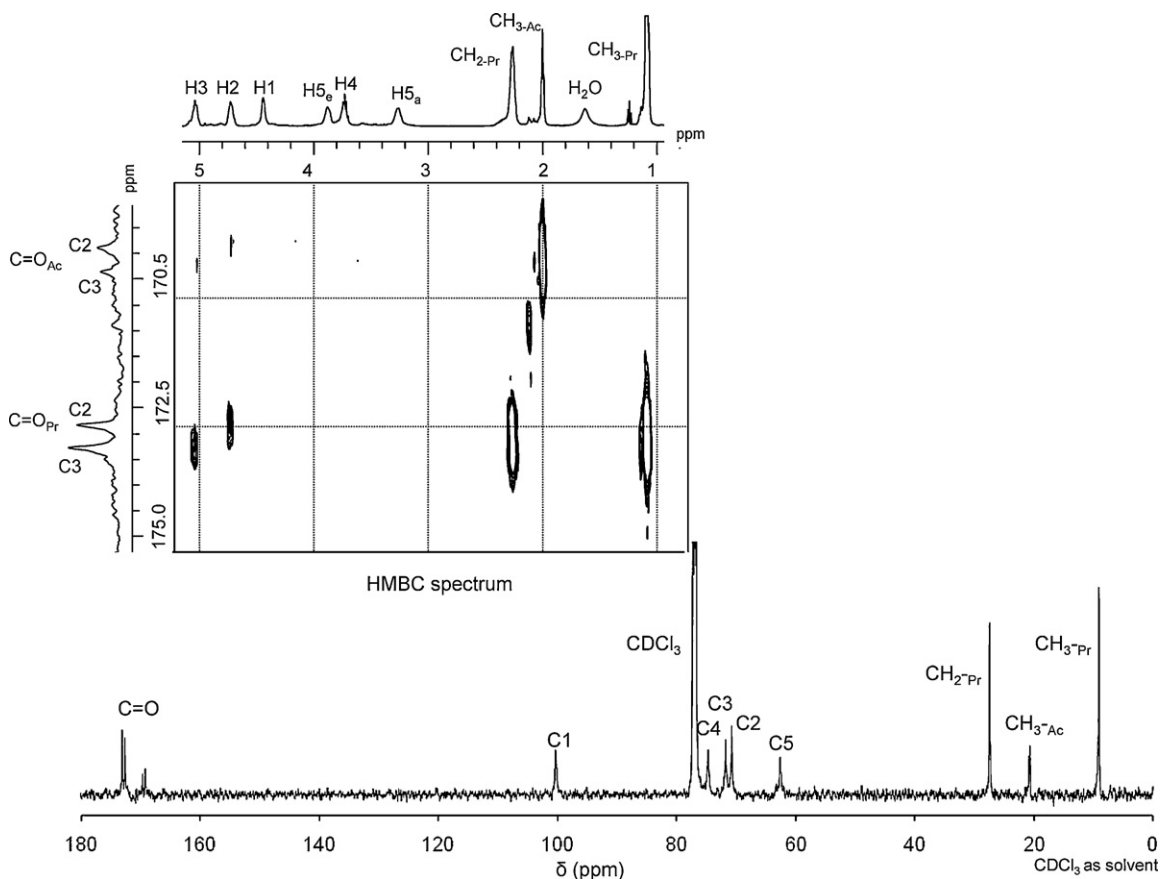
### 3.4. Solubility

Altering the molecular structure of xylan by introducing a hydrophobic acyl group changes its solubility property. In this study, the solubility behavior of xylan acetate and xylan acetate propionate having different DS values in CHCl<sub>3</sub> was investigated. Fig. 5 shows the solubility behavior of xylan acetate and xylan acetate propionate. The solubility of xylan acetate in CHCl<sub>3</sub> increases with an increase in DS. This is due to the increase in hydrophobicity of the polymer after acetylation. However, xylan

acetate remained partially soluble in CHCl<sub>3</sub> (~58%) even after complete acetylation (DS = 2.0). In certain case, fully acetylated cellulose is also partially soluble in CHCl<sub>3</sub> (Shaikh et al., 2009) and the use of mixed solvents provides better solubility (Bochek & Kalyuzhnaya, 2002). In the case of xylan acetate propionate, the solubility decreased with increase in the DS<sub>Ac</sub>. Xylan acetate propionate samples with DS<sub>Ac</sub> values of 0.6 and 1.1 were completely soluble in CHCl<sub>3</sub>. The sample with a DS<sub>Ac</sub> = 1.6 was still partially soluble in CHCl<sub>3</sub>. However, the solubility increased from 48% to 58%. This shows that the solubility of partially substituted xylan acetate is improved after perpropionylation.

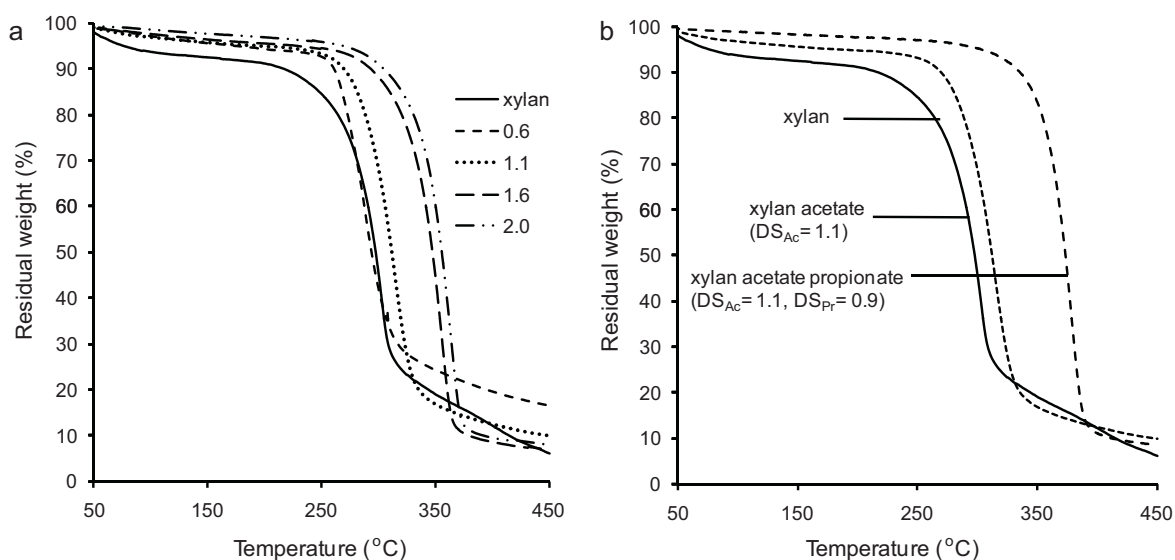
### 3.5. Electrospinning

In this study, xylan acetate nanofibers were formed by electrospinning method using HFIP a solvent. Xylan acetate with a DS = 2.0 can be electrospun into nanofibers. Xylan acetates with DS < 2.0 were not soluble in HFIP. Fig. 6 shows the SEM image of the as



**Fig. 3.** <sup>13</sup>C and expanded HMBC (embedded) NMR spectra of perpropionylated xylan acetate (DS<sub>Ac</sub> = 0.6, DS<sub>Pr</sub> = 1.4).





**Fig. 4.** TG thermograms of (a) xylan and xylan acetate with different DS and (b) xylan, xylan acetate ( $DS_{Ac} = 1.1$ ) and xylan acetate propionate ( $DS_{Ac} = 1.1$ ,  $DS_{Pr} = 0.9$ ). Xylan acetate propionate was obtained after perpropionylation of xylan acetate.

**Table 2**

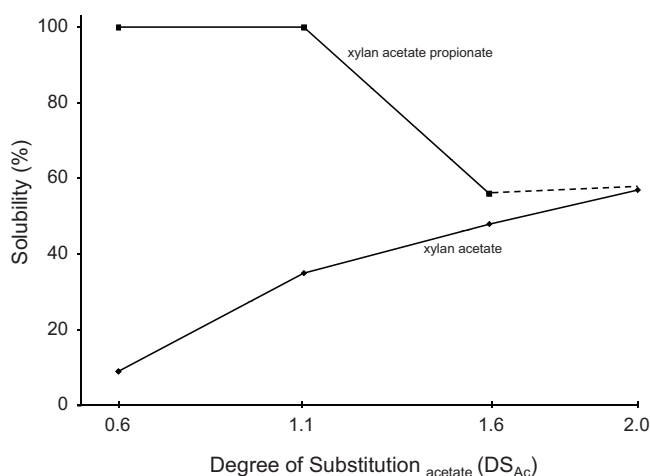
Mechanical properties of xylan acetate propionate films.

$DS_{Ac}$	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (GPa)
0.6	$48 \pm 3$	$10 \pm 2$	$0.6 \pm 0.1$
1.1	$46 \pm 3$	$8 \pm 2$	$0.8 \pm 0.1$

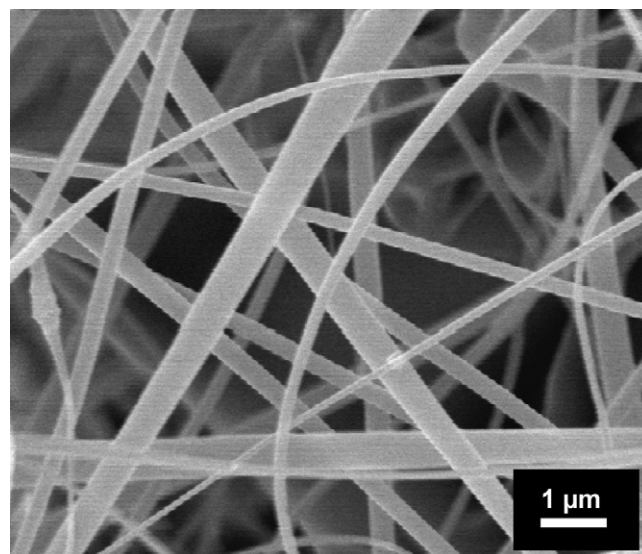
spun xylan acetate nanofibers with a  $DS = 2.0$ . At 10 wt./vol.-% xylan acetate, long beaded fibers were obtained after electrospinning at 30 kV. The diameter of the nanofibers ranged from 163 to 429 nm.

### 3.6. Mechanical characterization of xylan acetate propionate films

Xylan acetate propionate with a  $DS_{Ac}$  of 0.6 and 1.1 were made into films by solvent casting method. Table 2 shows the influence of DS on the mechanical properties of the films. Tensile test results revealed that the tensile strength of the xylan acetate films slightly decreased from 48 to 46 MPa with increase in  $DS_{Ac}$  from 0.6 to 1.1.



**Fig. 5.** Comparative solubility behavior of xylan acetate and xylan acetate propionate in  $CHCl_3$  (solution concentration: 20 mg/ml). Xylan acetate propionate was obtained after perpropionylation of xylan acetate.



**Fig. 6.** SEM image of as spun nanofibers prepared from xylan acetate ( $DS = 2.0$ ) in HFIP (10 wt./vol.-%).

In the case of elongation at break, the value slightly decreased from 10 to 8% when the  $DS_{Ac}$  increased from 0.6 to 1.1. This is due to the presence of lesser number of propionyl groups which makes the film less flexible. Consequently, this results in a more rigid film which is reflected in the increase in the value of the Young's modulus from 0.6 to 0.8 GPa.

## 4. Conclusion

Alkaline extraction of xylan from eucalyptus hardwood kraft pulp with 10% NaOH obtained a yield of 6–8%. Structural analysis of the isolated xylan revealed that it was a homoxylan. Acetylation of xylan was carried out in DMAc/LiCl/pyridine system at different reaction times in order to monitor the DS. Results revealed almost the same DS values at C-2 and C-3 positions of xylan acetate indicating the non-selectivity of the reaction.

The thermal stability of xylan, based on the TGA, was improved after acetylation. Likewise, the solubility of xylan in chloroform also

increased after chemical modification. Perpropionylation of partially substituted xylan acetate showed further increase in thermal stability and solubility. Xylan acetate with a DS = 2.0 can be electrospun into nanofibers. The mechanical properties of xylan acetate propionate films were dependent on the DS. The xylan propionate film having a lower DS<sub>Ac</sub> exhibited a higher tensile strength and elongation at break.

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