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Effect of acetylation on the material properties of glucuronoxylan from aspen wood

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Abstract

The effect of the degree of acetylation of glucuronoxylan on solubility, water content and thermal properties was investigated. Aspen glucuronoxylan, isolated by alkali extraction from wood chips, was acetylated to various degrees of substitution through reaction with acetic anhydride in formamide and pyridine by varying the reaction time. The degree of acetylation was determined by ^{1}H NMR spectroscopy. The molecular weight was decreased only to a small extent during the reaction, as seen by size exclusion chromatography. It was found that acetylation strongly affects the solubility properties as well as the equilibrium water content of the glucuronoxylans upon exposure to humidity. Samples with a high degree of acetylation are soluble only in aprotic solvents, whereas non-acetylated glucuronoxylan is partially soluble in hot water. In the same surrounding relative humidity, acetylated samples have lower water content than non-acetylated samples. Acetylation prevents thermal degradation, as shown by thermogravimetric analysis under nitrogen. Acetylation to a degree of substitution of 1.2 also results in a glass transition temperature, which we studied using differential scanning calorimetry, making it possible to thermoprocess acetylated glucuronoxylan.

Keywords: Acetylated glucuronoxylans; Glass transition; Thermal properties; Thermal stability; Water vapour sorption isotherms; Equilibrium water content

1. Introduction

There is an emerging need for renewable raw materials for a variety of applications such as disposable packaging, paper chemicals, thickeners, emulsifiers, absorbents and adhesives. Polysaccharides such as starch, pectins and hemicelluloses are produced by plants in vast quantities by the conversion of carbon dioxide and water using solar energy, which leads to a better carbon dioxide balance in our ecosystem. Starch is produced as an energy reserve in plants and has been converted into plastic materials by conventional thermoplastic processing (Shogren, Fanta, & Doane, 1993), often with glycerol as a plasticiser. Hemicelluloses are biosynthesised by the majority of plants but, in contrast to starch, hemicelluloses are not an energy reserve for the plant but act as a matrix material present between the cellulose microfibrils and as a linkage between cellulose and lignin (Popa, 1996). Hemicelluloses have not yet been used commercially for the preparation of polymeric materials.

One of the possible reasons for the lack of utilisation of hemicellulose as a material has been the shortage of access to high molecular weight hemicellulose on an industrial scale. For example, in traditional pulping processes designed for isolation of cellulose from wood, hemicelluloses are degraded to a low degree of polymerisation (Sjöström, 1993). Only recently was a pilot plant for the isolation of hemicellulose from plant tissue built at Virginia Tech, Blacksburg, USA (Gabrielii, Gatenholm, Glasser, Jain, & Kenne, 2000; Glasser, Jain, & Sjöstedt, 1995; Gustavsson et al., 2001). The procedure involves an alkali extraction resulting in deacetylated hemicellulose. Other processes for isolation of high molecular weight hemicellulose from agricultural sources are currently being developed (Buchanan et al., 2000).

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One drawback of hemicelluloses is their thermal properties. The decomposition temperature of wood hemicelluloses has been found to be lower than that of cellulose and lignin. (Ramiah, 1970; Shafizadeh and Chin, 1977). Native hemicellulose degrades at elevated temperatures in pyrolytic reactions involving cleavage of glycosidic bonds and dehydration to furfural and volatile low molecular products (Shafizadeh, McGinnis, & Philpot, 1972). The thermal stability of polysaccharides has been improved by esterification. Starch esters, for example, have been shown to have higher thermal stability than native starch (Aburto, Hamaili, Mouysset-Baziard, Senocq, Alric, & Borredon, 1999).

Hemicelluloses are heteropolysaccharides whose composition varies between different plant species. In hardwoods such as aspen, beech and birch, however, the hemicellulose consists chiefly of *O*-acetyl-(4-*O*-methyl-glucurono)xylan (Timell, 1967). The backbone consists of β-(1 → 4)-linked D-xylopyranosyl residues substituted with one α-(1 → 2)-linked 4-*O*-methyl-D-glucuronic acid per approximately every 10th such residue. The xylopyranosyl residues are partially acetylated in the C-2 and/or C-3 positions (Timell, 1967). The degree of acetylation in native aspen glucuronoxylan has been reported to be between 0.6 and 0.7 (Khan, Lamb, & Overend, 1990; Teleman, Lundqvist, Tjerneld, Stålbrand, & Dahlman, 2000). The reasons for acetylation in native glucuronoxylan are not clear and the effects of acetylation on material properties are not well documented.

Several chemical modifications of glucuronoxylans have been reported (Antal, Ebringerová, & Micko, 1991; Ebringerová, Novotná, Kacuráková, & Machová, 1996; Ebringerová, Sroková, Talába, Kacuráková, & Hromádková, 1998; Ebringerová, Alföldi, Hromádková, Pavlov, & Harding, 2000; Fang, Sun, Fowler, Tomkinson, & Hill, 1999; Sun, Fang, Tomkinson, & Hill, 1999a; Sun, Tomkinson, Liu, & Geng, 1999c; Sun, Fang, & Tomkinson, 2000; Sun, Fang, Tomkinson, Geng, & Liu, 2001) and have recently been extensively reviewed (Ebringerová and Hromádková, 1999). Different reaction procedures for acetylation of xylan have been described (Fang, Sun, Tomkinson, & Fowler, 2000; Gardner & Chang, 1974; Jain, Sjöstedt, & Glasser, 2000; Johnson, Fontana, & MacKenzie, 1988; Mitchell, Grohmann, Himmel, Dale, & Schroeder, 1990; Ramsden and Blake, 1997; Šimkovic and Alföldi, 1990; Sun, Fang, Tomkinson, & Jones, 1999b; Zinbo and Timell, 1965).

The aim of this study was to investigate the effect of acetylation on material properties, such as thermal properties, solubility and equilibrium water content. The synthesis of a gradient of acetylated glucuronoxylans and the study of their material properties will contribute to a better understanding of the role of acetylated glucuronoxylan in the cell wall.

2. Experimental

2.1. Material

The aspen glucuronoxylan used in this study was isolated by alkali extraction at the Department of Wood Sciences and Forest Products at Virginia Tech, Blacksburg, USA. The aspen wood chips (Rockhammar bruk, Sweden) were refined and the fibres prehydrolysed [0.05 M HCl/70 °C/2 h]. A lignin extraction was done [80% EtOH/1% w/w NaOH/80 °C/0.35 bar/2 h] after which the glucuronoxylan was extracted in two sequential steps [4% NaOH/ambient temperature and 14 h/70 °C and 2 h]. The glucuronoxylan was bleached [50% H_2O_2/40 °C/30 h/pH 11], neutralised, ultrafiltrated and spray dried. The exact separation procedure and the properties of the isolated polymer are described elsewhere (Gabrielii et al., 2000; Gustavsson et al., 2001).

2.2. Acetylation

Several different acetylation methodologies have been evaluated. We selected the method described by Zinbo and Timell (1965). Non-acetylated glucuronoxylan (5 g) was mixed with 130 g of formamide (Sigma-Aldrich F47671) for 24 h under continuous stirring at ambient temperature. The reaction was started by the addition of 200 ml of pyridine (Sigma-Aldrich F82704) and 67 ml of acetic anhydride (Prolabo 21390). The reaction was tested during various periods of time and then interrupted by the addition of 4 l of ice cold 2% hydrochloric acid (Sigma-Aldrich R30721). The precipitate was filtered through a Büchner funnel and washed twice with 600 ml of ice cold deionised water, twice with 600 ml of methanol (Prolabo 20847) and once with 600 ml of pentane (Sigma-Aldrich R32288).

Hydroxypropylation was followed by acetoxypropylation according to the method described by Jain et al. (2000). Glucuronoxylan (5 g) was dissolved in 20 ml of sodium hydroxide at pH 13 under nitrogen and magnetic stirring for 2 h. The solution was cooled in an ice bath before dropwise addition of 5 ml of propylene oxide. The reaction mixture was left at ambient temperature for 12 h under continuous stirring. After cooling, another 5 ml of propylene oxide was added. After 12 h at ambient temperature, the hydroxypropylated glucuronoxylan was precipitated in 150 ml of acetone, washed with acetone, filtered and dried in a vacuum oven. Acetoxypropylation was initiated by the dissolution of 4 g of hydroxypropylated glucuronoxylan in 20 ml of formamide under nitrogen. Acetic anhydride (10 ml) was added dropwise over a period of 1 h and the reaction mixture was stirred at ambient temperature for 12 h. Another 10 ml of acetic anhydride was added dropwise over 1 h followed by stirring at ambient temperature for 24 h and at 80 °C for 1 h before precipitation in 300 ml of 0.5 M hydrochloric acid. The product was washed in deionised water, filtered and dried in a vacuum oven.

Acetylation in lithium chloride/dimethylacetamide was done according to Sun et al. (1999a). Glucuronoxylan (0.6 g) was dissolved in 30 ml of 1% w/w lithium chloride/dimethylacetamide at 120 °C. The temperature was lowered to 85 °C and 4-dimethyl-aminopyridine (DMAP) (0.15 g), acetic anhydride (0.66 ml) and dimethylacetamide (10 ml) were added. Another addition was made after 5 h, and the reaction was left for 60 h before precipitation in four volumes of ethanol and washing in ethanol and acetone.

2.3. NMR Spectroscopy

For ^{1}H NMR analysis, a portion of the dried samples (1.6–2.7 mg) was dissolved in 0.6 ml of dimethyl-d_6 sulfoxide. A small amount (2 μl) of D_2O was added to exchange hydroxyl protons. ^{1}H NMR spectra were obtained at 400.13 MHz using a Bruker DPX400 spectrometer. The spectra were acquired at a probe temperature of 80 °C. The typical acquisition parameters employed were a 90° pulse, a spectral width of 6000 Hz and a repetition time of 17 s.

2.4. Size exclusion chromatography

Fully acetylated glucuronoxylan samples with reaction times of 90 min and 71 h, respectively, were saponified with ammonia and freeze dried. 30 mg of the sample was placed in a 50-ml round bottomed flask and 3 ml of ammonia solution (25%) was added. The flask was closed with a stopper plug. The plug was secured and the flask left in a fume hood overnight at ambient temperature. To remove the ammonia, some distilled water was added to the suspension and the liquid was removed using a rotary evaporator. After another addition of distilled water, the sample was freeze dried.

Size exclusion chromatography analysis was done with 0.05 M LiBr in DMSO:water (90:10) as the mobile phase. The following PSS (Polymer Standard Service) column set was used: GRAM 30, 100, 3000 (8 × 300 mm) and guard column (8 × 50 mm). The flow rate was 0.4 ml/min at 60 °C, resulting in a system pressure of 58 bar. The samples were dissolved in the eluent in a shaker for 24 h at room temperature and filtered using regenerated cellulose membranes (0.45 μm). An RI detector (Shodex RI-71), a two-angle laser light scattering detector (Precision detectors PD 2000) and a viscosimetric detector (Viscotek H502) were used for detection. The data were collected and calculated using WINGPC 6.0 software of PSS. Molar mass data were calculated from the viscosity and RI signals by universal calibration using pullulan standards (PSS). The amount of soluble material passing the column was determined by concentration calibration with xylopentaose as a standard.

2.5. Solubility

The solubility of the untreated and acetylated glucuronoxylan samples in chloroform (Sigma-Aldrich R32211), dimethylsulfoxide (Merck 1.02931.1000) and deionised water was studied. 10 mg of sample was mixed with 2 ml of solvent under magnetic stirring for 24 h. Chloroform was kept at ambient temperature, while DMSO and water were heated to 80 °C.

2.6. Water vapour sorption isotherms

The untreated and acetylated glucuronoxylan samples were ground in a mortal in liquid nitrogen and conditioned in closed vessels containing saturated salt solutions. The salts used were lithium chloride (Sigma-Aldrich R13013), magnesium chloride hexahydrate (Sigma-Aldrich R31413), magnesium nitrate hexahydrate (Sigma-Aldrich F63079), sodium chloride (Sigma-Aldrich F71381) and potassium sulphate (Sigma-Aldrich R31270) resulting in relative humidities of 11, 33, 54, 75 and 97%, respectively (ASTM, 2001). The equilibrium water content was measured gravimetrically on a Mettler AE260-DR balance and calculated as the weight of water in the sample compared to the total weight. The results are displayed as water vapour sorption isotherms and average values with standard deviations (95% confidence interval) at the highest surrounding relative humidity for the different degrees of acetylation (DS_{Ac}).

2.7. Thermal analysis

Thermogravimetric analysis (TGA) was used to study the thermal stability of the samples. The instrument used was a Perkin Elmer TGA7 and the temperature was increased from 45 to 600 °C with a heating rate of 10 °C/min in nitrogen atmosphere. Triplicates of about 2 mg of sample were run in each experiment and the data presented consist of average values of the temperature at which there is a 10% weight loss and standard deviations (95% confidence interval).

The thermal transitions of the samples were studied using differential scanning calorimetry (DSC). The instrument used was a Perkin Elmer DSC7 and the heating and cooling rates were 10 °C/min. Two subsequent heating scans were made and the glass transition temperature was calculated from the second heating scan. Before analysis, the glucuronoxylan samples were dried at 45 °C under vacuum over night. The samples were heated from 45 to 225 °C, cooled to 45 °C and then heated to 250 °C. The sample with $DS = 1.9$ was also studied by modulated DSC using a 2920 MDSC V2.5F, Universal V3.1E TA Instruments. The heating and cooling rates were 5 °C/min. The sample was heated from 0 to 240 °C, cooled to 0 °C and then heated to 280 °C.

3. Results and discussion

3.1. NMR spectroscopic characterization

^{1}H NMR spectra of some of the acetylated xylans are shown in Fig. 1. The signals at 2.0 ppm indicated that the polysaccharides are acetylated (Hirano, 1971; Teleman et al., 2000; Teleman, Tenkanen, Jacobs, & Dahlman, 2002). In the ^{1}H NMR spectra of the acetylated glucuronoxylans with shorter reaction time (Fig. 1(A) and (B)), several peaks were observed that were not found in the ^{1}H NMR spectrum with the largest proportion of acetyl signals. This is expected for partially acetylated xylan. Several (1 → 4)-linked β-D-xylopyranosyl structural elements in partially *O*-acetylated (4-*O*-methylglucurono)xylans isolated from hardwoods were recently identified: unsubstituted, 2-*O*-acetylated, 3-*O*-acetylated, 2,3-di-*O*-acetylated and [MeGlcA α-(1 → 2)][3-*O*-acetylated] (Teleman et al., 2000). A minor signal from the methyl group of 4-*O*-methylglucuronic acid at 3.45 ppm was observed in the ^{1}H NMR spectra (Teleman et al., 2000).

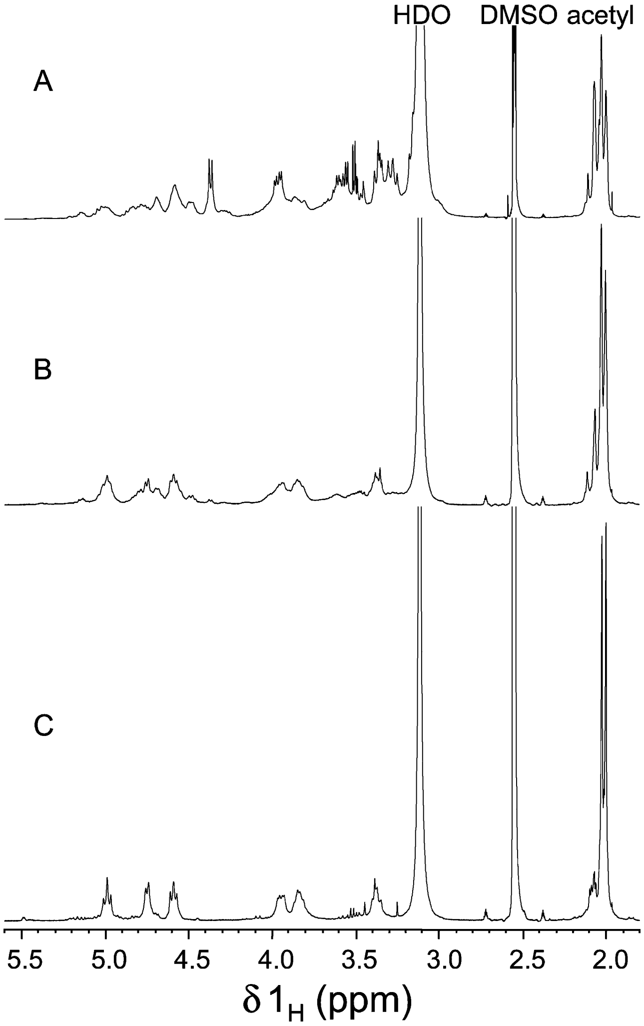

Fig. 1. ^{1}H NMR spectra of aspen 4-*O*-methylglucuronoxylan that has been acetylated. (A) $DS_{Ac} = 0.6$; (B) $DS_{Ac} = 1.2$; (C) $DS_{Ac} = 1.9$.

The degree of acetylation (DS_{Ac}) was determined from the relative intensities of the signals of the acetyl groups at 2.0 ppm and those of all carbohydrate signals. The following equation was used:

$$DS_{Ac} = \frac{(\text{Sum of integrals for acetyl groups at 2.0 ppm})/3}{(\text{Sum of integrals for carbohydrate signals at 3.2–5.6 ppm})/6}$$

3.2. Acetylation

The hydroxypropylation followed by acetoxypropylation according to Jain et al. (2000) and acetylation in lithium chloride/dimethylacetamide with acetic anhydride and DMAP described by Sun et al. (1999a) did not result in a fully acetylated glucuronoxylan. Acetylation in formamide/pyridine with acetic anhydride described by Zinbo and Timell (1965) did, however, and this procedure was therefore selected.

The reaction time was varied in order to obtain glucuronoxylans with a gradient of acetylation. The effect of the reaction time on the degree of acetylation as determined by NMR is shown in Fig. 2. The total reaction time used by Zinbo and Timell (1965) was 71 h, and three additions of acetic anhydride were made. According to our results, however, a much shorter time and only one addition of acetic anhydride are necessary to obtain a fully acetylated glucuronoxylan. The DS_{Ac} is 1.8 after only 90 min.

The molecular weight was not extensively decreased during the acetylation, as shown by

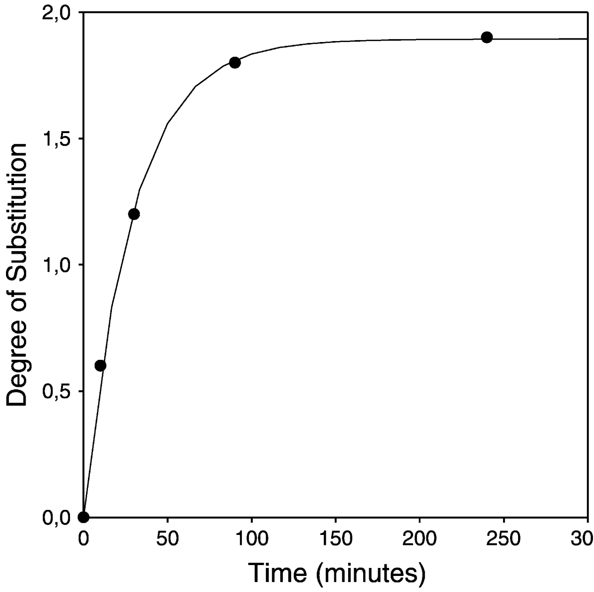

Fig. 2. The degree of substitution was controlled by varying the reaction time.

size exclusion chromatography. After 71 h, the mass average molecular weight decreased from 15,600 to 13,600.

3.3. Solubility

The solubility of glucuronoxylan in chloroform, DMSO and deionised water was investigated. These solvents were chosen because of the difference in polarities. The acetylation strongly affects the solubility of the glucuronoxylan in different solvents, shifting from the non-acetylated glucuronoxylan and the one with $DS_{Ac} = 0.6$ that are partially soluble in hot water to the fully acetylated glucuronoxylan that is soluble in nonpolar solvents such as chloroform. All samples could be dissolved in the polar aprotic solvent DMSO.

3.4. Equilibrium water content

The water content of a biopolymer affects for example its thermal properties and mechanical properties as water acts as a plasticiser. Fig. 3 shows water vapour sorption isotherms for the glucuronoxylans with various degrees of acetylation. The unmodified glucuronoxylan is very hygroscopic and quickly adapts its water content to the surrounding humidity. The hysteresis between the adsorption and desorption has been observed previously for hemicellulose (Christensen and Kelsey, 1958). The equilibrium water content in a defined surrounding relative humidity decreases with increasing DS_{Ac}. Fig. 4 shows the equilibrium water content in a surrounding relative humidity of 97%. The average values are calculated from triplicates and the standard deviations are marked in the diagram (95% confidence interval). The non-acetylated glucuronoxylan has a water content of 31% w/w at equilibrium, the sample with $DS_{Ac} = 0.6$ has a water content of 24% w/w, the one with $DS_{Ac} = 1.2$ contains 17% w/w water and the fully acetylated glucuronoxylan contains 10% w/w water. Acetylation makes the glucuronoxylan less sensitive to humidity by allowing fewer sites for hydrogen bonding with the water molecules.

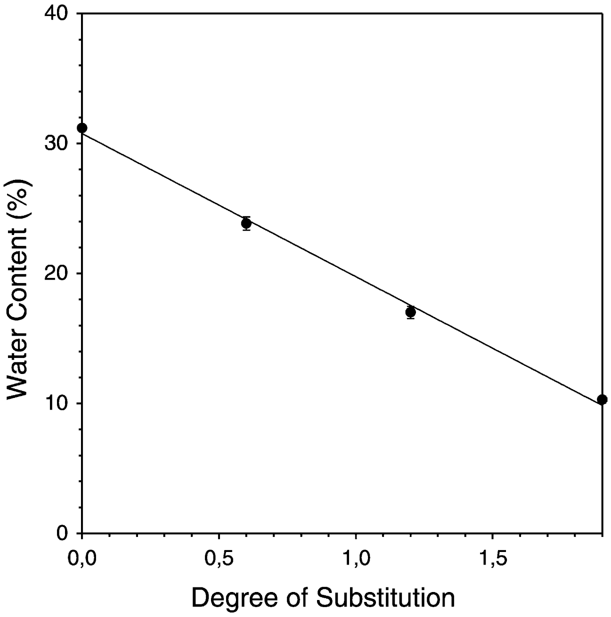

Fig. 4. Equilibrium water content as a function of DS_{Ac} at 97% surrounding relative humidity.

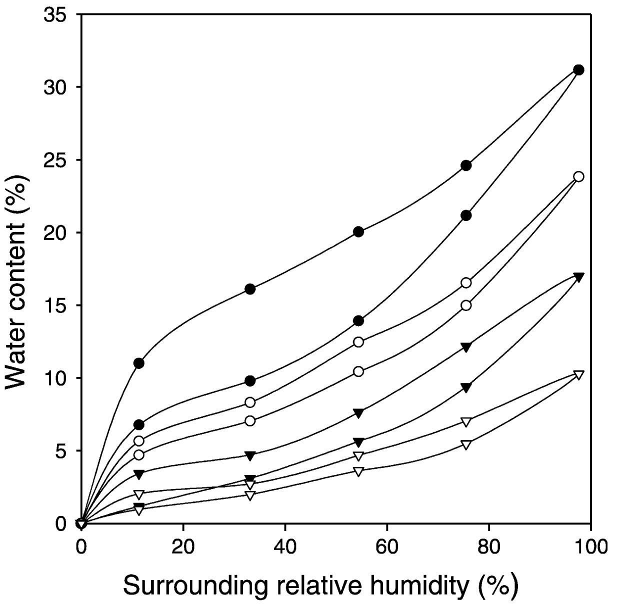

Fig. 3. Water vapour sorption isotherms at 20 °C for glucuronoxylans with different DS_{Ac}. (● $DS_{Ac} = 0$, ○ $DS_{Ac} = 0.6$, ▼ $DS_{Ac} = 1.2$, ▽ $DS_{Ac} = 1.9$).

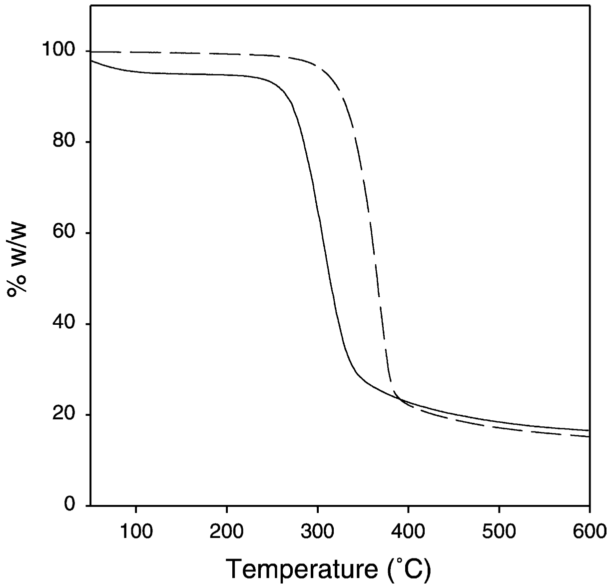

Fig. 5. TGA of non-acetylated (solid line) and fully acetylated (dashed line) glucuronoxylan.

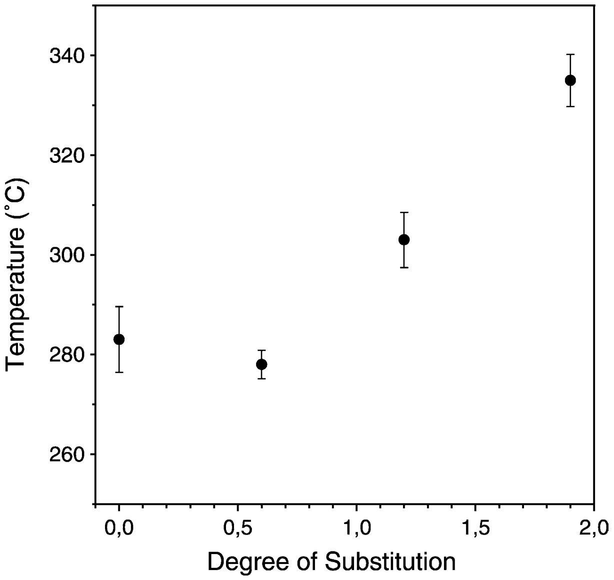

Fig. 6. Temperature at which the weight loss is 10% w/w, during a TGA scan under nitrogen, as a function of DS_{Ac}.

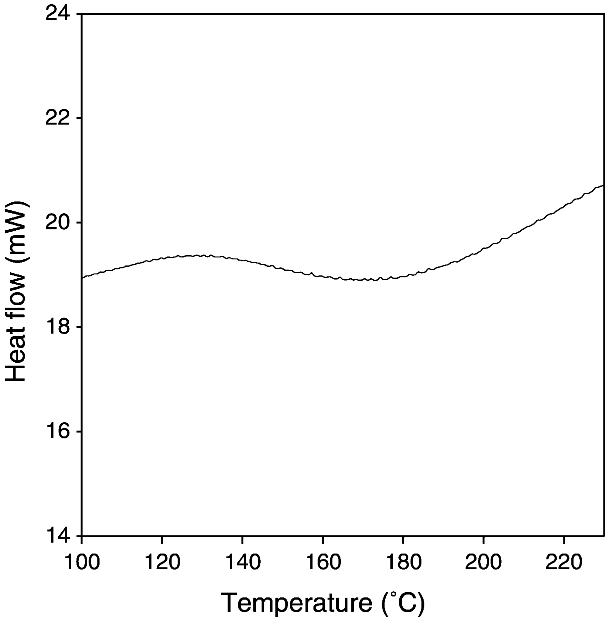

Fig. 7. DSC heating scan of non-acetylated glucuronoxylan.

3.5. Thermal properties

The thermal stability of the glucuronoxylans, investigated using TGA, was measured as the weight loss of the sample as the temperature was increased, see Fig. 5. The weight of the sample is dramatically reduced when the polymer degrades thermally.

In the non-acetylated sample, the onset of thermal degradation takes place at a lower temperature than in the acetylated samples, see Fig. 5. The thermal stability is improved by acetylation, as can be seen in Fig. 6. The temperature at which there is a 10% w/w weight loss is 283 °C for non-acetylated glucuronoxylan and 335 °C for the fully acetylated sample. A possible explanation is that water in the samples promotes hydrolysis through 4-*O*-Me-glucuronic acid, which speeds up the process of decomposition. Since the acetylated samples contain less water, this mechanism is not very pronounced.

DSC was used to study the thermal transitions of the glucuronoxylans. The non-acetylated glucuronoxylan and the acetylated glucuronoxylan with $DS_{Ac} = 0.6$ did not show any glass transition temperature (T_g), and degraded thermally during the heat scan. Fig. 7 shows that there is an endotherm starting at around 100 °C because there is some water in the samples. At high temperatures (>250 °C) the heat flow increases upon increasing temperature. Such behaviour is related to thermal decomposition. The TGA measurements also show that thermal decomposition to furfurals and volatile low molecular weight products starts in this temperature region.

The glucuronoxylan with $DS_{Ac} = 1.2$ has a very clear glass transition, however, as is shown in Fig. 8. Between 160 and 200 °C, the heat flow is increased to a higher level, indicating a glass transition temperature. The T_g was considerably lower in the second heat scan than in the first. This behaviour has been observed before (Rindlav-Westling, 2002) and can be related to the phenomenon of water becoming available in the amorphous regions and plasticising the material. The hydroxyl groups of the glucuronoxylans form hydrogen bonds with the water, instead of between the chains, which gives the polymer increased mobility. The reason why the acetylated glucuronoxylan with $DS_{Ac} = 1.2$ has a T_g and the glucuronoxylan with

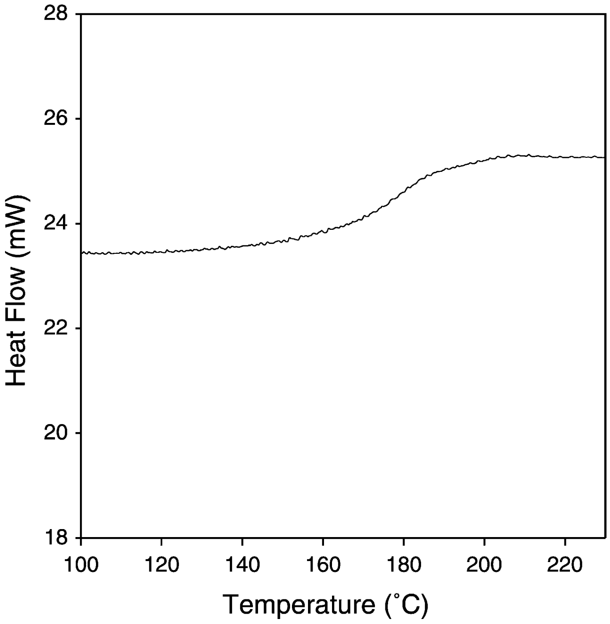

Fig. 8. DSC scan (second heating scan) of acetylated glucuronoxylan with $DS_{Ac} = 1.2$.

lower DS_{Ac} does not is that the acetyl groups prevent the polymer chains from forming hydrogen bonds and thus increase the mobility of the chains.

No clear T_g could be observed when the fully acetylated sample was heated in the DSC. The sample was thus studied using modulated DSC. A vague transition in the same region as for the sample with $DS_{Ac} = 1.2$ was detected. In this case as well, the T_g was considerably lower in the second heat scan than in the first.

Films were formed when the acetylated glucuronoxylans, which have a T_g, were heated under greater pressure. This is not the case in the non-acetylated sample.

4. Summary of results

Glucuronoxylan with a gradient of acetylation can be prepared by selecting the reaction time at which the acetylation is done in formamide/pyridine through a reaction with acetic anhydride. Acetylation of glucuronoxylan strongly affects the solubility properties, shifting from the non-acetylated glucuronoxylan, which is partially soluble in hot water, to fully acetylated glucuronoxylan, which is soluble only in aprotic solvents such as chloroform and DMSO. The water content in a defined surrounding relative humidity is strongly decreased with a higher degree of acetylation, as the possibilities of forming hydrogen bonds is decreased.

The thermal stability of glucuronoxylan, as shown by TGA, is improved by acetylation. The temperature at which 90% w/w of the sample remains increases from 283 to 335 °C. DSC showed that dry non-acetylated glucuronoxylan and glucuronoxylan with a DS_{Ac} in the same range as native glucuronoxylan degrades, but that samples with a DS_{Ac} of 1.2 or higher have a glass transition temperature. Acetylation results in a thermo-processable glucuronoxylan, which was confirmed by making films under elevated temperature and pressure.

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