

BIRCH XYLAN GRAFTED WITH PLA BRANCHES OF PREDICTABLE LENGTH

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Birch xylan (4-*O*-methylglucuronoxylan) isolated from a kraft cooking liquor was delignified and grafted with polylactide of predictable branch length. This graft copolymerization resulted in very high total yields, greater than 90%, and with less than 10% polylactide homopolymer byproducts. Mild reaction conditions (40°C, 5 to 120 minutes) were used, which was believed to limit transesterification reactions and thus make it possible to reach good predictability of the polylactide branch length. The thermal properties of the polylactide-grafted xylan depended on the branch length. Short branches resulted in fully amorphous materials with a glass transition temperature of about 48 to 55°C, whereas long polylactide branches resulted in semi-crystalline materials with melting points of about 130°C. Using mixtures of L-lactide and D/L-lactide in the monomer feed further altered the thermal properties. The degradation temperatures of the polylactide-grafted xylylans were higher than that of the unmodified xylan, with degradation temperatures of about 300°C and 250°C, respectively. Tensile testing showed increased elongation at break with increasing branch length. The proposed method thus enables tailor-making of copolymers with specific thermal and mechanical properties.

Keywords: Hemicellulose; Xylan; Grafting; Lactide; ROP; Glass transition; Melt transition; Tensile strength

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INTRODUCTION

Grafting of birch xylan (4-*O*-methylglucuronoxylan) with polylactide (PLA) is one way of producing a thermoprocessable, biodegradable material made entirely from renewable resources.

Hardwood xylan has gained interest as a novel product from the kraft pulping process due to new methods of isolation, which give a high molecular mass xylan with high purity (Dahlman *et al.* 2008). Xylan is an extremely abundant hemicellulose (Simson and Timell 1978; Sjöström 1993; Timell 1967), which is dissolved in kraft cooking liquors and is usually burned in the recovery boiler giving very little energy contribution. Apart from its potential as a strengthening agent in paper (Dahlman *et al.* 2003; Ebringerová *et al.* 1994; Mobarak *et al.* 1972; Ribe *et al.* 2010; Walker 1965), xylan is interesting for applications in packaging materials. Xylan is however highly sensitive to water and moisture, has poor film-forming ability, and lacks thermal processability. Modification is one route to overcome these limitations in material

properties and add value to the xylan. For example, acylation of xylan increases its hydrophobicity and thermal processability (Fang *et al.* 1999; Fundador *et al.* 2012). Xylan acylated with lauroyl chloride has also been shown to form rather elastic films (Chaa *et al.* 2008). Acylation by the grafting of lactide is one modification that gives a product derived completely from renewable resources. Such acylation on pullulan has been reported by Donabedian and McCarthy (1998) and more recently on birch xylan by us (Persson *et al.* 2012).

In order to tailor lactide-grafted xylans with specific thermal and mechanical properties, a synthesis that leads to a predictable length of the lactide branches attached to the xylan backbone is preferred. The grafting method previously reported by us (Persson *et al.* 2012) for xylan modification however lacked predictability of the PLA branch length when grafting long PLA branches onto xylan. Birch xylan contains 5 to 10% of uronic acids (Simson and Timell 1978), which will probably inhibit the ring-opening polymerization (ROP) of the lactide. Moreover, the high temperature and long reaction times needed for the copolymerization when employing the conventional stannous octanoate catalyst probably limited the predictability of the PLA branch length.

The concept of graft-copolymerization of PLA has been evaluated for numerous polysaccharides as potential components in blends with PLA (Donabedian and McCarthy 1998; Feng and Dong 2007; Gong *et al.* 2006; Lee *et al.* 2006, Liu *et al.* 2004; Lonnberg *et al.* 2006; Wu *et al.* 2005; Yuan *et al.* 2007). Recently, PLA-grafted hemicelluloses were reported as good compatibilizers in blends of wood hydrolysates and PLA (Saadatmand *et al.* 2011). However, there are few reports of good predictability of the PLA branch lengths. The grafting of propargyl-terminated PLA onto a xylan derivative has recently been made with usage of click chemistry, providing good predictability of the PLA branch lengths; however it requires a three-step synthesis. (Enomoto-Rogers and Iwata 2012). The use of stannous octanoate as catalyst often results in a large amount of PLA homopolymer due to transesterification reactions (Chen *et al.* 2005). Good predictability of the branch length has been reported for PLA grafting from chitosan using triethylamine as catalyst (Liu *et al.* 2004; Wu *et al.* 2005), but with total yields of less than 50%. Other amine-containing catalysts that have shown to be effective for the ROP of lactide are dimethylaminopyridine (DMAP) (Saadatmand *et al.* 2011; Nederberg *et al.* 2001), carbene (Nyce *et al.* 2002), and guanidine (Zhang *et al.* 2010). The most effective catalyst according to the literature is the guanidine-based triazobicyclodecene (TBD) (Pratt *et al.* 2006).

In the present paper, TBD has been used to catalyze the graft copolymerization of PLA onto birch xylan. The reaction scheme is shown in Fig. 1. The hypothesis was that, with this highly effective catalyst, a short reaction time and a low reaction temperature could be used. This would limit transesterification reactions and the formation of byproducts like PLA homopolymer and result in a higher predictability of the PLA branch length. This effective catalyst was also expected to increase the total yield due to high lactide conversion into copolymer. PLA-g-xylan copolymers with predictable PLA branch lengths could then be synthesized for evaluation of the effect of branch length on the thermal and mechanical properties. These properties could be further modified by using mixtures of lactide stereoisomers in the monomer feed, resulting in PLA branches with different configurations.

The high predictability and configuration control of the PLA branches permits the tailoring of PLA-g-xylan copolymers with specific thermal and mechanical properties.

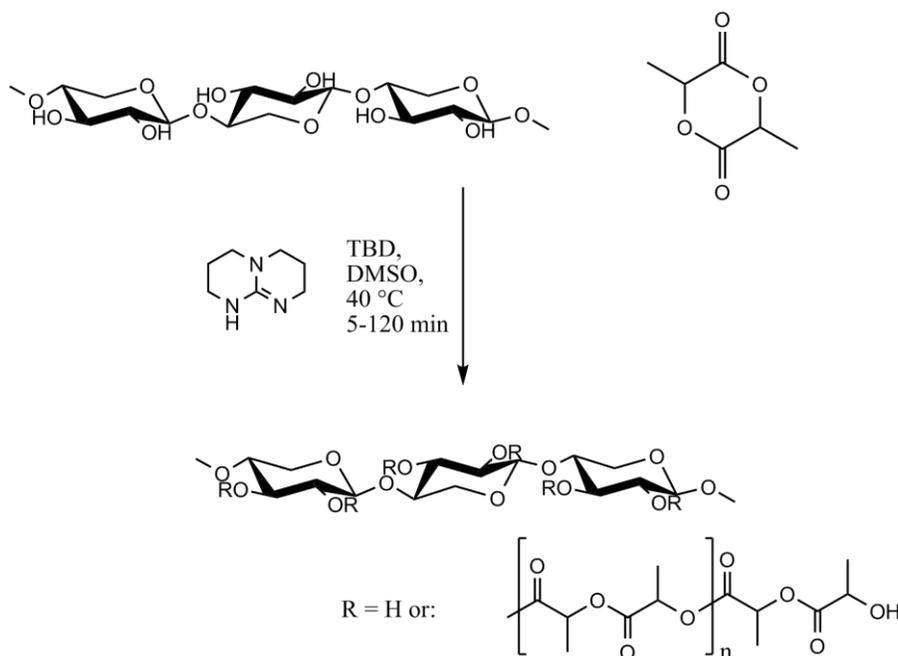


Fig. 1. Reaction scheme of the graft-copolymerization of PLA onto xylan

EXPERIMENTAL

Materials

Birch xylan was isolated from a kraft cooking liquor by ultrafiltration and subsequent precipitation in methanol according to the method described earlier by Dahlman *et al.* (2008). After freeze-drying, the xylan consisted of 84%-wt xylan, 1%-wt other carbohydrates, and 15%-wt lignin according to carbohydrate and lignin analysis.

The freeze-dried xylan was delignified with sodium chlorite. Xylan (60 g) was mixed with a solution of sodium acetate in water (33%-wt, 600 mL). The mixture was adjusted to pH 4 with acetic acid. Sodium chlorite (60 g) was added and the reaction was stirred at room temperature overnight. The delignified xylan was washed with an ethanol:water mixture (4:1, 4 x 250 mL) and subsequently freeze-dried and stored under reduced pressure over phosphorous pentoxide. After delignification, the xylan content was increased to 99%-wt. with less than 1%-wt. lignin. The content of 4-*O*-methylglucuronic acid residues on the xylan was 5%-wt.

The DMSO solvent was dried over molecular sieves with vigorous stirring at 80°C and degassed under vacuum for 30 minutes before use. L-lactide and D/L-lactide (Sigma-Aldrich) were recrystallized from ethyl acetate, filtered, dried under vacuum, and stored at reduced pressure over phosphorus pentoxide before use. Triazabicyclodecene (TBD) (Sigma-Aldrich) was stored under reduced pressure over potassium hydroxide and otherwise used as received.

Methods

Synthesis of PLA-g-xylan copolymers

The standard Schlenk technique was used for all the syntheses. All glassware was dried in an oven at 200°C overnight and cooled in a desiccator over phosphorus pentoxide before connection to the Schlenk line.

Xylan (10 mg to 1 g) and lactide (1 to 15 g) were dissolved in DMSO (2 to 15 mL) at 80°C in a sealed reaction flask. Monomer mixtures of L-lactide (0 to 100 wt-% of total lactide) and D/L-lactide racemic mixture (0 to 100 wt-% of total lactide) were used. The reagent mixture was treated with three cycles of vacuum and N₂ (g) under vigorous stirring to remove any moisture. After cooling to 40°C, TBD dissolved in DMSO (60 mg/mL) was added. The reaction was quenched (10 min to 2 h reaction time) by adding benzoic acid dissolved in THF or DMSO (100 mg/mL; Benzoic acid:TBD = 1:1 molar eq.).

The PLA-g-xylan copolymers were isolated by precipitation in deionized water and subsequently purified by dialysis against water to remove DMSO, catalyst, and unreacted L-lactide and D/L-lactide. The copolymers were freeze-dried and stored in a desiccator over phosphorus pentoxide. The isolated yield was calculated according to Equation 1:

$$\text{Yield (wt\%)} = \frac{\text{Total mass after reaction}}{\text{Total mass of starting material}} \times 100\% \quad (1)$$

A theoretical molar mass was also calculated for each synthesis according to,

$$M_t = DP_{xyl} \times \left(\frac{n_{La}}{n_{xyl}} \times M_{La} + M_{xyl} \right) \quad (2)$$

where DP_{xyl} was calculated from SEC-measurements of the delignified birch xylan as M_w/M_{xyl} , n_{La} and n_{xyl} is the molar amount of lactide and xylose units added in the feed, M_{La} is the molar mass of one lactide unit, and M_{xyl} is the molar mass of one xylose unit.

Chemical analyses

Lignin determination: The lignin content prior to and after delignification of the birch xylan was determined after acid hydrolysis as described in the TAPPI-standard (TAPPI 2009). The total lignin content was determined as the acid-insoluble residue (Klason lignin), determined gravimetrically, together with the acid-soluble residue, which was determined spectrophotometrically at 205 nm.

Carbohydrates and uronic acids: The carbohydrate composition and content of uronic acids in the xylan starting material was determined by enzymatic hydrolysis followed by capillary zone electrophoresis (CE). The method has previously been described in detail (Dahlman *et al.* 2000). Prior to the CE analysis, the sugars in the hydrolysates were derivatized with 4-aminobenzoic acid ethyl ester, which enabled quantification by UV absorption at 306 nm. The CE system employed was a Beckman P/ACE MDQ capillary electrophoresis system (Beckman Coulter, Inc., Fullerton, CA,

USA) equipped with a diode-array UV detector. An uncoated fused-silica capillary column was used, and the conditions were those described previously (Dahlman *et al.* 2000).

Molar mass analyses: Aqueous size exclusion chromatography (SEC) was employed for the molar mass analyses of unmodified xylan according to the method previously described by Jacobs and Dahlman (2001). Pre-filtered samples (1 mg dry matter) were injected into the SEC system consisting of three columns (Ultrasphere SEC 120, 250, and 500, Waters Assoc. USA). The system was calibrated by MALDI-TOF-MS measurements on fractionated xylan samples (Jacobs and Dahlman 2001). Aqueous sodium acetate/hydroxide (100 mM/100 mM) was used as eluent. The signal from the refractometer was processed with PL Cirrus 3.1 SEC software and interface (Polymer Laboratories Ltd., UK). Employing SEC with a THF eluent system determined the molar mass averages of the PLA-g-xylan copolymers. The SEC system consisted of three columns (Styragel HR1, HR4E, and HR 5E; Waters Assoc. USA) and was calibrated with polystyrene standards. The signal from the refractometer was processed using the PL Cirrus 3.1 SEC software and interface (Polymer Laboratories Ltd., UK).

¹H NMR: Prior to the NMR studies, the samples were dissolved in d₆-DMSO (20 mg/mL). A NMR spectrometer working at 400.13 Hz (Bruker) was used. Thirty pulses were employed at a spectral width equivalent to 16 Hz and a delay time (D1) of 1.65 s. Four dummy scans and at least 16 scans were utilized for each sample. Topspin software (Bruker) was used for the acquisition and processing of data. The degree of polymerization (DP) of the PLA branches was calculated according to,

$$DP_{La-NMR} = \frac{I_{1.2} + I_{1.5}}{3} \bigg/ 2 \times I_{4.2} \quad (3)$$

where DP_{La-NMR} is the average number of lactide units per PLA branch, $I_{1.5}$ is the integral intensity for the signal derived from the internal methyl protons at 1.5 ppm, $I_{1.2}$ is the integral intensity for the signal derived from the terminal methyl protons at 1.2 ppm, and $I_{4.2}$ is the integral intensity for the signal derived from the terminal methine protons at 4.2 ppm. An example of a ¹H NMR spectrum of a PLA-g-xylan is shown in Fig. 2. The ratio was divided by 2 in order to calculate the DP of PLA in the chain and not the number of lactic ester units. The DP was also used to calculate the average molar mass of the PLA-g-xylan copolymers:

$$M_{calc-NMR} = DP_{xyl} \times (DP_{La-NMR} \times DS_{La-NMR} \times M_{La} + M_{xyl}) \quad (4)$$

where DP_{xyl} was calculated from SEC-measurements of the delignified birch xylan as M_w/M_{xyl} , DP_{La-NMR} is the DP of the PLA chains calculated from Eq. 3, DS_{La-NMR} is the number of substituted OH-groups per xylose unit, M_{La} is the molar mass of one lactide unit, and M_{xyl} is the molar mass of one xylose unit. Full conversion of the xylan hydroxyls to PLA chains was assumed, and DS_{La-NMR} was therefore set to 2.

Evaluation of material properties

Preparation of films: For solution casting, PLA-g-xylan (2 g) was dissolved in THF or chloroform (15 mL) before being cast on a petri dish. The solvent was evaporated in a fume hood overnight at room temperature, after which the film was peeled off. The thicknesses of the thin films were between 0.15 and 0.20 mm.

For compression moulding, PLA-g-xylan (4.0 g) was molded in a 0.5 mm thick frame at 80°C and 300 bar for 10 minutes. The instrumentation used for compression molding was a Polystat 200 tabletop press from Servitec, Germany.

Thermal analyses: The thermal degradation properties were evaluated by thermogravimetric analysis (TGA). A Perkin Elmer TGA7 instrument was used with a flow rate of the purge gas (He) of 20 to 35 mL/min and of the balance purge gas (N₂) of 40 to 60 mL/min. The sample (4 mg) was dried at 105°C for 20 min prior to heating at a rate of 15°C/min to 300°C.

Differential scanning calorimetry (DSC) was used to determine the glass transition temperature (T_g) and melting point (T_m). A Waters DSC Q1000 V9.4 Build 287 instrument was used. Each sample (2 to 5 mg) was transferred into the pan used for DSC measurements, dried at 105°C for four hours, and cooled to room temperature in a desiccator before being put in the DSC instrument. The samples were equilibrated at 0°C before heated to 200°C at a rate of 3°C/min and then rapidly cooled to 0°C before a second heating cycle under the same conditions.

Tensile Testing: Young's modulus, maximum tensile stress, and fracture strain were measured using a Zwick Z010 tensile tester, controlled by a textXpert 7.1® computer program supplied from Zwick GmbH & Co (Germany). Testing was performed in accordance with the ISO standard method (ISO 1993) at 23°C and 50% RH. At least 5 dumbbell-shaped specimens (ISO 2005) were punched from each film.

RESULTS AND DISCUSSION

Delignified birch xylan isolated from a kraft cooking liquor was grafted with PLA by ROP of lactide using TBD as catalyst. Pure L-lactide or mixtures of L-lactide and D/L-lactide (racemic mixture) were used. The resulting graft-copolymers were denoted L(No.) or D/L(No.) depending on the lactide stereoisomer used in the feed. The number in brackets is the weight average molar mass (M_w) in kDa.

Synthesis of PLA-g-xylan

Birch xylan was grafted with PLA by ROP of lactide. TBD was chosen as the catalyst because of its high reactivity (Kiesewetter *et al.* 2009). The short reaction times and low temperature needed when using TBD were expected to limit transesterification reactions and the formation of PLA homopolymer. The synthesis was evaluated for predictability of the PLA branch length, the polydispersity, and the formation of PLA-g-xylan or PLA homopolymer, using different reaction parameters such as reaction time, temperature, and catalyst amount.

Table 1 shows the weight average molar mass (M_w), polydispersity (PD), DP of the PLA branches, the isolated yield and amount of PLA homopolymer present for the

unmodified xylan, and three high molar mass PLA-g-xylans synthesized using different reaction times. An increase in reaction time resulted in a higher M_w and lower PD. The high M_w value and high yield suggested a very high conversion of the L-lactide.

The decrease in PD with increasing degree of conversion was in agreement with the results reported by Pratt *et al.* (2006) and was explained by the high activity of the catalyst. The reaction time needed for high molar mass PLA-g-xylan was longer than that required for the synthesis of pure PLA using a similar monomer/initiator ratio (Pratt *et al.* 2006). The slower reaction was probably due to the use of DMSO as solvent and the lower mobility of xylan compared to that of a low molar mass initiator such as benzyl alcohol.

Table 1. Reaction Parameters, Weight Average Molar Mass (M_w), Polydispersity (PD), Isolated Yield, and Amount of PLA Homopolymer of PLA-g-xylans Synthesized using Different Reaction Times

Sample	La:Xyl:TBD (molar fraction)	Reaction Time (min)	Reaction Temp. (°C)	M_w (kDa)	PD	DP _{La NMR}	Yield (%-wt)	PLA homopol. (%)
xyl	-	-	-	12.5	1.19	-	-	-
L(757)	102:1:0.3	5	42	757	1.20	25	99	30
L(784)	102:1:0.3	30	42	784	1.19	16	96	27
L(1070)	102:1:0.3	120	42	1070	1.14	47	85	37

The length of the PLA branches could be predicted from the La:xylan molar ratio in the feed, when the catalyst amount was not more than 30%-mole with respect to xylan repeating units. This is shown in Table 2, as the achieved M_w was between 60% and 80% of the theoretical molar mass (M_t). Too large an amount of catalyst led to a broadening of the molar mass distribution. Short reaction times were needed in the synthesis of lower molar mass PLA-g-xylans in order to achieve a predictable PLA branch length and low PD. This is also shown in Table 2, where the achieved M_w is considerably higher than the M_t of sample L (143), even though a shorter reaction time was employed. Longer reaction times in this case led to transesterification and a broadening of the molar mass distribution. The reaction parameters, degree of polymerization (DP), and molar mass averages and polydispersity (PD) for some of the PLA-g-xylans synthesized are listed in Table 2.

^1H NMR was used to calculate the branch length (DP) of the grafted PLA. The ^1H NMR spectra of the unmodified xylan and PLA-g-xylan L(143) are shown in Figure 2. From the branch length, an average molar mass was calculated and compared to the number average molar mass (M_n) measured by SEC. These values agreed quite well considering that the SEC calculations were based on polystyrene standards, which probably had hydrodynamic properties different from those of the PLA-g-xylan copolymers. It was not possible to estimate the DS of PLA-g-xylans because of the very small signals from xylan protons in the spectra, as seen in the ^1H NMR spectrum of L(143) in the bottom of Fig. 2. Because of the high reactivity of the catalyst, the calculated average molar mass was based on a DS of 2.

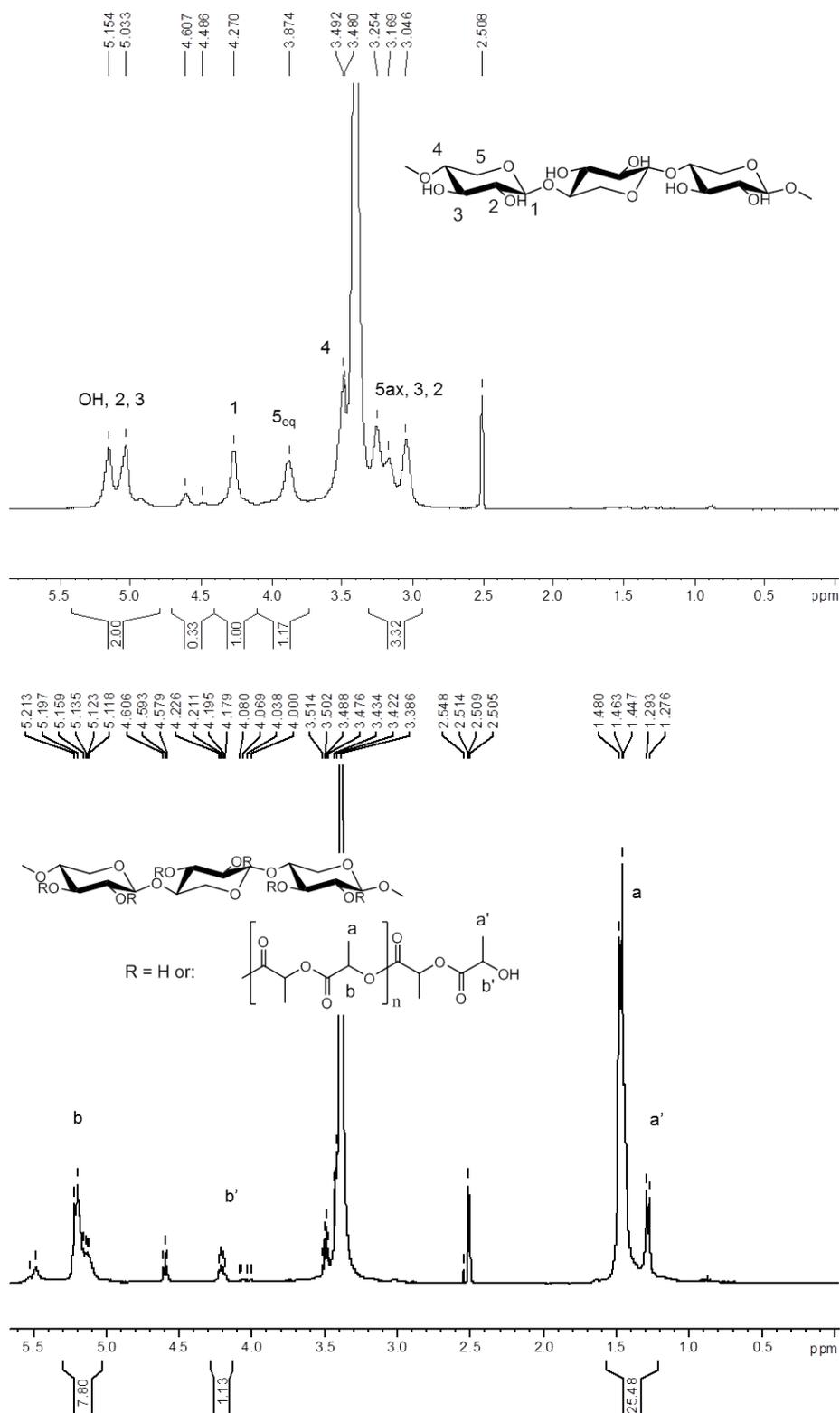


Fig. 2. ¹H NMR spectra of unmodified xylan (top) and PLA-g-xylan L(134) (bottom)

Table 2. Reaction Parameters, DP, Molar Mass Averages, PD, Theoretical Molar Mass (M_t), Isolated Yield, and Amount of PLA Homopolymer of PLA-g-Xylans Measured by ^1H NMR and SEC

Sample	La:Xyl:TBD (molar fraction)	Reaction Time (min)	DP_{La} NMR	$M_{\text{calc.}}$ NMR (kDa)	M_n (kDa)	M_w (kDa)	PD	M_t (kDa)	Yield (%-wt)	PLA homopol. (%)
L(143)	5:1:0.24	35	4	153	103	143	1.39	81	88	0
L(294)	23:1:0.53	120	12	331	158	294	1.86	326	102	0
L(359)	51:1:0.71	120	13	367	231	359	1.56	708	73	9
L(475)	60:1:0.17	120	18	490	392	475	1.21	831	104	10
L(1070)	102:1:0.30	120	43	1170	938	1070	1.14	1400	85	37

The formation of PLA-g-xylan and PLA homopolymer could be followed by SEC measurements. The chromatograms showed two peaks, of which one could be assigned to the PLA homopolymer by MALDI-TOF-MS analysis. Figure 3 shows the SEC chromatogram of PLA-g-xylan L(359), and the small peak due to PLA homopolymer. The amounts of homopolymer formed during the syntheses, calculated as the relative height of the homopolymer peak in the SEC chromatogram, were in most cases less than 10%, as shown in Tables 2 and 3.

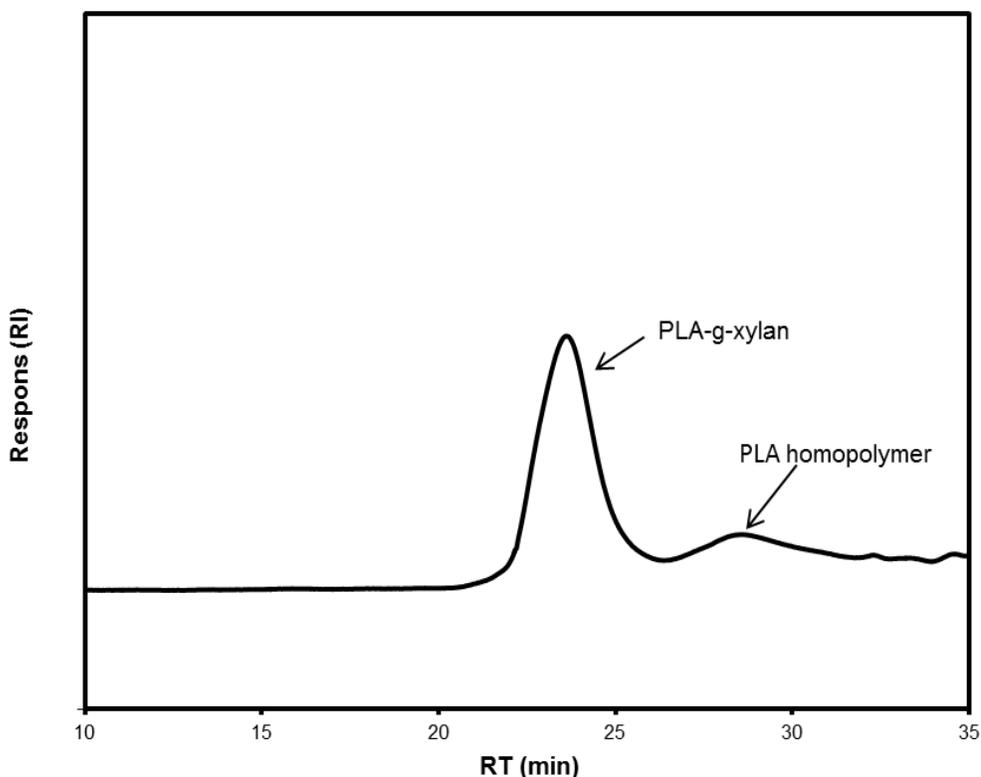


Fig. 3. SEC chromatogram of L(359) showing the formation of PLA-g-xylan copolymer as compared to PLA homopolymer

In order to alter the material properties of the high molar mass PLA-g-xylans, the configuration of the PLA branches was varied by adding the stereoisomer D/L-lactide (racemic mixture) to the monomer mixture. Table 3 shows the amount of D/L-lactide added and the M_w , M_t , isolated yield and PD of these syntheses. The syntheses showed good predictability of the PLA branch length with an M_w between 50% and 70% of the theoretical M_t . The isolated yield for the first four samples listed in Table 3 was above 100%. This could be due to DMSO residues trapped in the samples. Because of this, these four samples were not subjected to further material analyses. A slightly lower M_w was achieved when 100% D/L-lactide was used in the monomer feed, suggesting that the D/L-lactide was less susceptible to ROP than the L-lactide.

Table 3. M_w , PD, M_t , Isolated Yield, and Amount of Homopolymer Formed for PLA-g-xylans Synthesized with Different Proportions of D/L-lactide in the Monomer Feed

Sample*	La:Xyl:TBD (molar fraction)	D/L of total La in feed (%-wt)	DP _{La} NMR**	M_w (kDa)	PD	M_t (kDa)	Yield (%-wt)	PLA homopol. (%)
D/L(711)	73:1:0.35	5	n.a.	711	1.26	1010	105	2
D/L(746)	76:1:0.36	10	n.a.	746	1.18	1050	112	14
D/L(700)	73:1:0.35	20	n.a.	700	1.24	1010	135	12
D/L(630)	73:1:0.35	100	n.a.	630	1.27	1010	131	0
D/L(650)	95:1:0.66	5	15	650	1.37	1310	66	5
D/L(766)	99:1:0.67	10	17	766	1.42	1360	102	8
D/L(755)	99:1:0.67	20	18	755	1.40	1360	99	7
D/L(584)	95:1:0.68	100	n.a.	584	1.53	1310	97	8
* The reaction time was between 120 and 140 min and the reaction temperature was 42°C for all samples.								
** n.a. = not analyzed.								

Thermal Properties

Choosing different branch lengths of the PLA could alter the thermal properties. All PLA-g-xylans showed thermoplastic properties with a repeatable glass transition temperature (T_g) in the range of 47 to 55°C, which is comparable with the reported T_g for pure poly(L-lactide) of 55 to 60°C (Engelberg and Kohn 1991). An M_w above 400 kDa was needed for detection of a melting temperature (T_m) of 130°C (+/-5) in the DSC curve of PLA-g-xylans made by grafting of pure L-lactide. This PLA branch length, gained by a molar excess of 50:1 (L-lactide:xylan), thus led to side-chain crystallization and a semi crystalline PLA-g-xylan. In comparable results with PLA-grafted chitosan, a molar excess greater than 10:1 was needed for melting transitions (Liu *et al.* 2004). This indicates that the thermal properties are highly dependent on the polysaccharide used for PLA grafting.

Earlier reported T_m values for pure poly(L-lactide) were about 155°C (Engelberg and Kohn 1991) compared to 130°C for the PLA-g-xylans produced. A similar decrease in T_m has been reported for starch-grafted poly(L-lactide) by Chen *et al.* (2005),

suggesting that the physical properties of the graft copolymer were very different from those of the pure homopolymer.

The thermal properties of the high branch length PLA-g-xylans could be further altered by adding D/L-lactide to the monomer mixture. With 10% of D/L-lactide in the PLA branches, the T_m decreased to about 110°C. PLA-g-xylans made with 20% and 100% D/L-lactide became fully amorphous with no detectable T_m and with T_g 's of 50°C and 40°C, respectively. Figure 2 shows the DSC curves for the unmodified xylan and PLA-g-xylans L(134), L(534), L(1070), and D/L(755). Except for the unmodified xylan, all DSC curves showed repeatable T_g in two heating cycles. Figure 2 also shows that, with increasing branch length, the PLA-g-xylans went from being fully amorphous (L(134)) to semi-crystalline in the first heating cycle (L(534)) to semi crystalline in both heating cycles (L(1070)). In addition, with 20% D/L-lactide in the monomer mixture, a PLA-g-xylan with high branch length again was fully amorphous (D/L(755)).

The PLA-g-xylans showed degradation temperatures (T_d) of 280 to 320°C, compared to the unmodified xylan with a T_d of 250°C and earlier reported values for PLA homopolymer of 240 to 255°C (Engelberg and Kohn, 1991). This showed that the graft-copolymerization had no negative effect on the T_d values compared to any of the individual homopolymers.

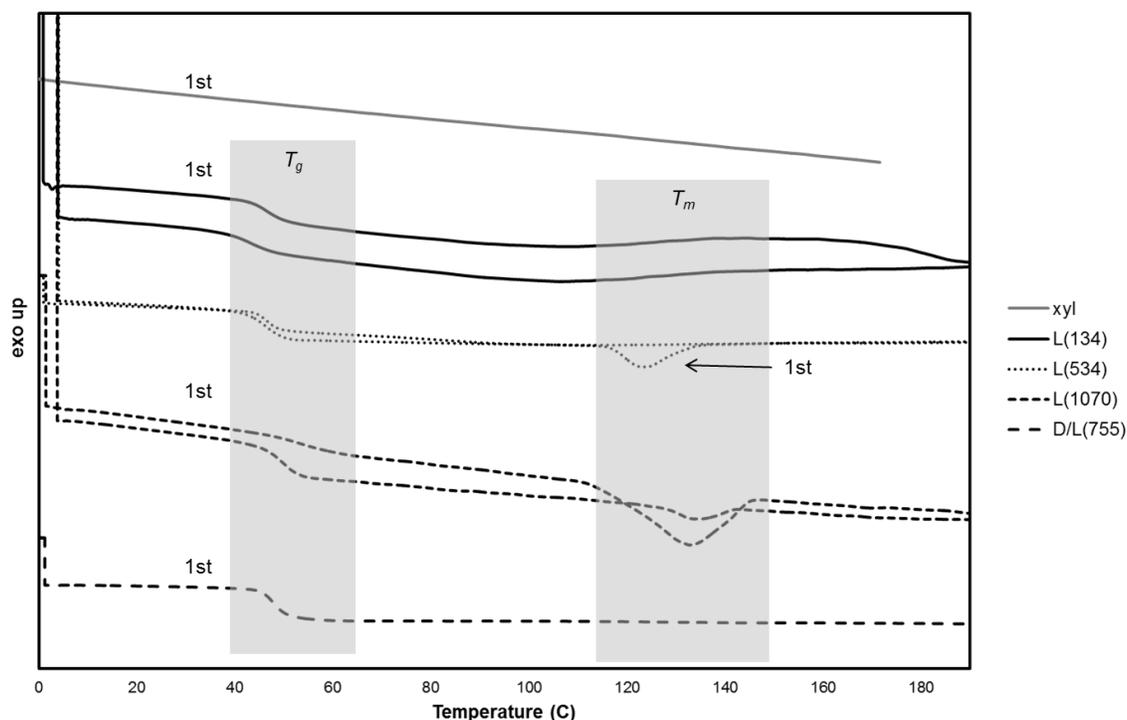


Fig. 3. DSC curves of the unmodified xylan and some of the PLA-g-xylans showing different thermal properties depending on PLA branch length and configuration. The pre-dried sample was heated from 0 to 200°C at 3°C/min, quenched to 0°C and then reheated to 200°C at 3°C/min. Reported T_g and T_m for pure poly(L-lactide) has been from 55 to 60°C and 155°C, respectively (Engelberg and Kohn 1991)

Tensile Strength Properties

All of the PLA-g-xylans could be compression-molded into clear films. However, only the PLA-g-xylan made from 20% of D/L-lactide could be subjected to tensile testing since the other films were too brittle. The results are shown at the bottom of Table 4. The D/L-lactide in the PLA branches thus acted as a built-in softener. The PLA-g-xylan synthesized from 100% D/L-lactide became very sticky upon compression molding and could not be tested for tensile strength properties.

Table 4. Tensile Strength Properties of Solution-Cast Thin Films from the PLA-g-Xylans

Sample	% D/L	M_w (kDa)	DP_{La} _{NMR}	E-Modulus (MPa)	F_{max} (MPa)	Elongation _{break} (%)
L(134)*	0	134	4	320 (+/-50)	5.7 (+/-0.80)	9.3 (+/-1.7)
L(143)*	0	143	4	380 (+/-37)	7.9 (+/-1.1)	19 (+/-4.7)
L(294)**	0	294	12	180 (+/-23)	4.4 (+/-0.59)	100 (+/-22)
L(359)**	0	359	13	100 (+/-19)	3.0 (+/-0.40)	88 (+/-7.4)
L(534)**	0	534	n.a.	640 (+/-100)	2.5 (+/-0.34)	1.2 (+/-1.1)
D/L(650)**	5	650	15	130 (+/-43)	4.1 (+/-1.0)	130 (+/-22)
D/L(766)**	10	766	17	55 (+/-7.5)	3.5 (+/-0.38)	190 (+/-18)
D/L(755)**	20	755	18	74 (+/-18)	3.7 (+/-0.36)	180 (+/-34)
D/L(584)**	100	584	n.a.	87 (+/-28)	3.8 (+/-1.5)	120 (+/-22)
D/L(755)***	20	755	18	390 (+/-76)	2.9 (+/-0.99)	0.94 (+/-0.35)
* Solution casted thin films made from THF.						
** Solution casted thin films made from CHCl ₃ .						
*** Compression molded film.						
n.a. = not analyzed.						

All the PLA-g-xylans synthesized could be solution-cast into clear thin films, using THF or chloroform as solvent. Tensile tests on these thin films, shown in Table 4, indicated a greater elongation at break with increasing PLA branch length. This agrees well with previous results on short branch length lactide-grafted xylan reported previously (Persson *et al.* 2012). PLA-grafted polysaccharides used in various blends with PLA have also been shown to act as softeners, since they increase the ductility of thin films (Saadatmand *et al.* 2011; Chen *et al.* 2005; Ouchi *et al.* 2003). All the film samples listed in Table 4 were made from fully amorphous copolymers except for samples D/L(650) and D/L(766) which were semi-crystalline. The semi-crystalline

sample made from 100% L-lactide, L(534), became very brittle with an elongation at break of only 1%. Again, this showed that the D/L-lactide in the PLA branches acted as a built-in softener for samples D/L(650) and D/L(766). Furthermore, the results for sample D/L(755) indicate that the method for producing the films very much affects the tensile strength properties. Upon compression molding, this sample was considerably more brittle than the solution-cast film made from the same sample.

These results showed that the established method could be used for the synthesis of PLA-g-xylans with a predictable branch length, which enables the tailoring of copolymers with specific desired thermal and mechanical properties.

CONCLUSIONS

1. Birch xylan was grafted with PLA to give copolymers with predictable branch length.
2. PLA branches from oligomer length to polymer length could be grafted onto xylan in high yield with very small amounts of PLA homopolymer byproducts by utilizing mild reaction conditions. This was done by employing the highly effective triazobicyclodecene (TBD) catalyst.
3. The thermal properties and the tensile strength properties of the PLA-g-xylan depended on the PLA branch length, which was easily tuned.
4. Further modification of the thermal properties was achieved by altering the configuration of the PLA branches.
5. We have thus presented an easy one-step method for the PLA grafting of xylan with a predictable length of the PLA branches.

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