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Toward an alternative compatibilizer for PLA/cellulose composites: Grafting of xyloglucan with PLA

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ABSTRACT

Poly(L-lactic acid) (PLLA) chains were grafted on xyloglucan substrates via ring-opening polymerization of the L-lactide monomer. Different parameters such as the nature of the substrate (native or modified xyloglucan) and the substrate/monomer ratios were varied in the synthesis to achieve different lengths of the grafted chains. A range of experimental techniques including infrared spectroscopy and nuclear magnetic resonance were used to characterize the final product. Thermal analysis showed that the glass transition temperature of xyloglucan was decreased from 252 °C to 216 °C following the grafting of PLLA. The grafting of less hydrophilic chains from xyloglucan also affected the interaction with water: the PLLA-grafted xyloglucan was insoluble in water and the moisture uptake could be decreased by about 30%. Xyloglucan adsorbs strongly to cellulose; therefore such a graft copolymer may improve the compatibility between cellulose fibers and PLLA. The PLLA-grafted xyloglucan may be useful as a novel compatibilizer in fiber-reinforced PLLA composites.

1. Introduction

The utilization of natural renewable polymers is a promising topic in an ecological and economical context (Fomin & Guzeev, 2001; Gandini, 2008). Among bio-resourced polymers, one of the most important polymers is poly(lactic acid) (PLA) (Drumright, Gruber, & Henton, 2000; Garlotta, 2001). PLA is a semi-crystalline thermoplastic with good mechanical properties and exists in two sterio isomeric forms- poly (L-lactic acid) and poly(D-lactic acid)-conventionally represented as PLLA and PDLA respectively. Moreover, it is fairly hydrophobic, at least compared with most polysaccharides. PLA is derived from annually renewable resources and is used in the automobile and packaging industries, which consume a major portion of the global plastic production (Auras, Harte, & Selke, 2004; Garlotta, 2001). Recent advances in polymerization techniques pave the way for a more economic production of PLA, and broaden its uses (Datta & Henry, 2006; Lim, Auras, & Rubino, 2008). Reinforcement of PLA with plant fibers is an important area of research in the automobile industry and also in electronics applications (Bogoeva Gaceva et al., 2007; Mohanty, Misra, & Drzal, 2002). However, the hydrophilic nature of cellulosic plant fibers makes them difficult to disperse in the PLA matrix. Therefore, different compatibilizers were tried to make the hydrophilic fiber reinforcement compatible with the more hydrophobic polymeric matrix. Ideally the compatibilizer has a fiber-binding domain, which has a strong adhesion to the fibers, and one domain which interacts with the polymer matrix, for instance by physical entanglements. Among different classes of commercially available compatibilizers, maleic anhydride-grafted PLA has been thoroughly investigated (Carlson, Nie, Narayan, & Dubois, 1999; Plackett, 2004). The resulting composites have enhanced elastic modulus; however, no appreciable improvement in toughness (Plackett, 2004). A recent study on silane-modified cellulose nanocrystals in PLLA showed strong effects of the compatibilizer on the crystallization kinetics (Pei, Zhou, & Berglund, 2010).

Recently, a polysaccharide derived from seeds of the tamarind tree (*Tamarindus indica*) – xyloglucan (XG) – was envisaged as a high performance biopolymer in various applications (Kochumalayil, Sehaqui, Zhou, & Berglund, 2010; Mishra & Malhotra, 2009). XG is a non-food-based polysaccharide from an inexpensive waste resource, which is of interest for further commercial exploitation. XG is a primary cell-wall constituent in plants with a function to physically link cellulose microfibrils. Its cellulose backbone structure renders a strong affinity to cellulose fibers (Gidley et al., 1991; Kochumalayil et al., 2010; Urakawa, Mimura, & Kajiwara, 2002). This property has been used to improve the mechanical properties of paper (Lima, Oliveira, & Buckeridge, 2003) and cellulose-based aerogels (Sehaqui, Salajková, Zhou, & Berglund, 2010).

In the present work, PLLA chains are grafted from XG to form covalent bonds between the macromolecules with an ultimate

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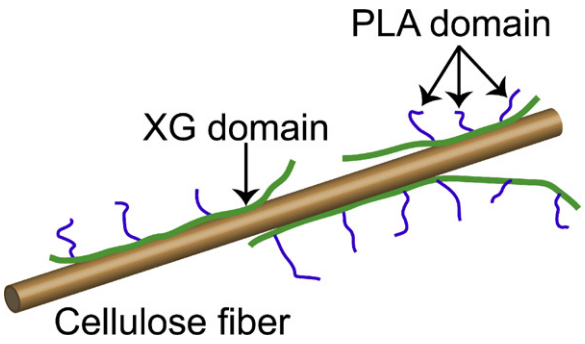

Fig. 1. Schematic representation of PLLA-grafted XG adsorbed to the surface of a cellulose fiber.

aim of preparing a novel graft copolymer compatibilizer for cellulose fiber/PLLA composites. The resulting material will have a fiber-binding domain based on XG and a polymer-binding domain of grafted PLLA chains (see Fig. 1). Recently, grafting of polymethyl methacrylate (PMMA) on XG was performed using polymethyl ceric ion-initiated polymerization (Mishra & Malhotra, 2012).

Among different possible grafting procedures, a 'grafting from' approach is used in the present study, where the polymerization is initiated from the surface of XG and the PLLA chains grow by addition of monomers. Ring-opening polymerization (ROP) is a technique used for the polymerization of cyclic monomers and has been successfully used for grafting PLLA chains onto cellulose surfaces (Lonnberg et al., 2006; Yuan, Yuan, Zhang, & Xie, 2007). The present study will focus on the use of a ROP technique to graft PLLA chains from XG. The study will investigate different polymerization conditions and effects from the XG substrate structure. To our best knowledge, this type of approach has not previously been used to prepare a high molar mass graft copolymer compatibilizer for PLLA. The advantage is that the polysaccharide may physically adsorb to the cellulose surface, similarly to XG/cellulose interfaces in the native state in the primary cell wall of plants.

2. Experimental

2.1. Materials

Xyloglucan (industrially purified, having a weight-average molecular mass of around 1.5 MDa, and containing nearly 10% impurities, mostly proteins) was provided by Innovassynth Technologies Ltd. (India) and was purified following a standard procedure (Kochumalayil et al., 2010). In a related experiment, XG was enzymatically treated to partially remove galactose by using β-galactosidase (from *Aspergillus oryzae*, Sigma Aldrich) (Kochumalayil et al., 2010; Shirakawa, Yamatoya, & Nishinari, 1998). The extent of galactose removal was around 30% compared to the amount present in native XG as obtained from high performance anion-exchange chromatography with pulsed amperometric detection (HPACEPAD) analysis of xyloglucooligosaccharides and the procedure details are reported elsewhere (Baumann et al., 2007; Kochumalayil et al., 2010). L-Lactide (LLA), obtained from Sigma Aldrich, was recrystallized from dry toluene. Chloroform ($CHCl_3$), methanol (MeOH), benzyl alcohol and tin(II) ethylhexanoate ($Sn(Oct)_2$) were purchased from conventional suppliers and used as received.

2.2. Grafting of XG via ROP of LLA

PLLA chains were grafted from XG surfaces following the procedure: XG (0.5 g) and recrystallized LLA (25 g) were dissolved into a round-bottom flask containing dry toluene (around 40 mL). The sacrificial initiator, benzyl alcohol, was added (60 μL for a target DP of 300) and the flask was then sealed with a rubber septum and degassed by three vacuum/argon cycles. The mixture was stirred and heated to 110 °C, and subsequently the catalyst, $Sn(Oct)_2$, was added (0.4 mL). The polymerization reaction was allowed to proceed for about 2 h and proton nuclear magnetic resonance (^{1}H NMR) was used to estimate the conversion of the monomer. In order to achieve a compromise between a minimized extent of trans-esterification reactions, and to maintain fairly high conversion, the reactions were stopped at a conversion of around 90%. Due to the presence of benzyl alcohol, free PLLA chains are formed during the reaction, the length of which is assumed to be the same as the grafted chains (Lonnberg et al., 2006). The PLLA chains were analyzed with ^{1}H NMR and size exclusion chromatography (SEC). Fig. 2 shows a simplified scheme of the reaction.

2.3. Characterization

2.3.1. Fourier transform infrared spectroscopy (FTIR)

FTIR was performed on a Perkin-Elmer Spectrum 2000 FTIR equipped with a MKII Golden Gate, Single Reflection ATR system from Specac Ltd, London, UK. The spectral range was 600–4000 cm^{-1}. The spectra were normalized against a specific ATR crystal absorption, allowing a comparison between the spectra.

2.3.2. Proton nuclear magnetic resonace (^{1}H NMR)

^{1}H NMR spectra were recorded on a Bruker AM 400 using $CDCl_3$ as solvent. The solvent signal was used as an internal standard. The conversion of the polymerization reaction was estimated from the signals at 5.2 ppm (—CH(CH_3)O—, polymer repeating unit) and 5.0 ppm (O—CH, monomer). The molecular weights (M_n) of the free PLLA were estimated from the degrees of polymerization (DPs) obtained from ^{1}H NMR. The DPs were calculated from the signals at 5.2 ppm (—CH(CH_3)O—, repeating unit) and 4.3 ppm (—CH(CH_3)OH, end group) (Janata et al., 2003).

2.3.3. Size exclusion chromatography (SEC)

SEC was used to determine the molecular weights and polydispersity index values of the PLLA formed during the ROP. The polymers were analyzed with a Verotech PL-GPC 50 Plus

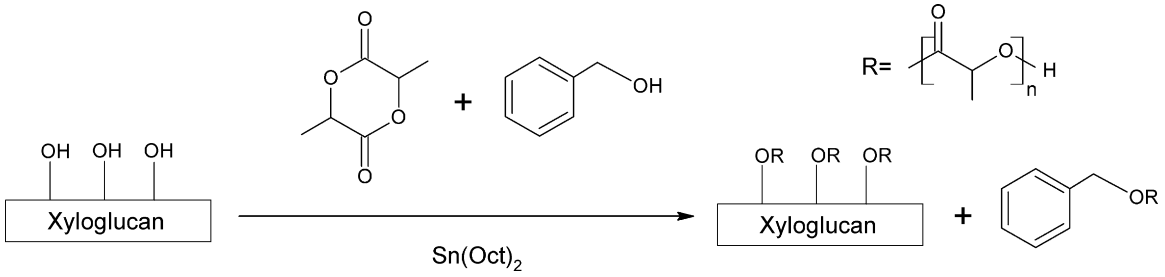

Fig. 2. Simplified scheme of the ROP reaction leading to the grafting of PLLA chains from XG substrate, using $Sn(Oct)_2$ as a catalyst and benzyl alcohol as a sacrificial initiator.

system equipped with a PL-RI Detector and two Polar Gel-M Organic (300 mm × 7.5 mm) columns from Varian. The samples were injected with a PL-AS RT Autosampler for PL-GPC 50 Plus and THF was used as mobile phase (1 mL/min, 35 °C). The calibration was carried out using polystyrene standards with a narrow molecular weight distribution. Corrections for the flow rate fluctuations were made using toluene as an internal standard. Cirrus™ GPC Software was used to process data.

2.3.4. Thermogravimetric analysis (TGA)

TGA was conducted on a Mettler Toledo TGA/SDTA851 instrument. STAR software was used to process the data. The samples were heated from 40 °C to 650 °C, using a heating rate of 10 °C/min, in a N_2 flow of 20 mL/min.

2.3.5. Differential scanning calorimetry (DSC)

DSC analysis was performed on a Mettler Toledo DSC 820 equipped with a Mettler Toledo Sample Robot TSO801RO calibrated using standard procedures. The XG samples were heated to 120 °C and equilibrated for 10 min to erase any previous thermal history, and thereafter cooled down to −70 °C. After equilibration, the samples were heated to 310 °C, at a heating rate of 10 °C/min and under a N_2 flow of 60 mL/min. The PLLA samples were heated to 220 °C and equilibrated for 2 min for the same purpose, and thereafter cooled down to 25 °C. After equilibration, the samples were heated up to 220 °C at a heating rate of 10 °C/min and under a N_2 flow of 20 mL/min.

2.3.6. Dynamic vapor sorption (DVS)

The moisture sorption isotherms of different samples were obtained using a DVS instrument from Surface Measurement Systems apparatus. Samples were dried in the DVS cell and the relative humidity (RH) in the DVS cell was increased in steps from dry state up to 95% RH. The samples were weighed at different RH atmospheres. The moisture content (M) at a particular RH level was calculated on a dry (or total weight) basis, as represented by:

$$M = \left[\frac{W_w - W_d}{W_d}\right] \times 100 \quad (1)$$

where M is the moisture content (%) in the material, W_w is the weight of the sample in the DVS cell when the moisture content has reached equilibrium, and W_d is the weight of the dried sample.

3. Results and discussion

3.1. Grafting of PLLA from XG via ROP

The grafting of PLLA was performed on native tamarind-seed XG and modified XG using a 'grafting from' approach. The modified XG has been exposed to galactoxidase enzymes so that the number of galactose side groups in XG is 30% reduced (see Section 2). The degree of polymerization (DP) of the PLLA chains is given by the ratio of monomer to initiating groups. Two different target DPs were used in the present work: DP150 and DP300.

Fig. 3. Native XG (left vial) and PLLA-grafted XG (right vial) in water, after stirring and heating at 60 °C for 2 h.

Since the number of initiating hydroxyl groups on XG is unknown, a sacrificial initiator (benzyl alcohol) was added to the reaction system to control the reaction. This co-initiator system has already been investigated as an efficient method for ROP of lactides (Kricheldorf & Damrau, 1997; Lonnberg et al., 2006; Trollsas et al., 2000).

The target DP was based only on the monomer/free initiator ratio, not taking into account the unknown number of initiating groups on the surface of the substrate. Thus, the theoretical molecular weight calculated in each case was higher than the ones obtained by NMR or SEC.

The data in Table 1 show the real average molar mass of free PLLA as measured by NMR and SEC, and these data are lower than the theoretical values. It was reported that ROP using stannous octoate as catalyst was sensitive to water (Schwach, Coudane, Engel, & Vert, 1997). Thus, despite all measures taken to avoid water, the hydrophilic nature of XG resulted in the presence of some traces of water in the system. The residual water can also function as initiating sites for the ROP of PLLA, resulting in lower average molecular weights and higher PDI values of the formed polymer. The partial degalactosylation of XG (modified XG) slightly improved the grafting efficiency, as PLLA grafted on modified XG shows the highest molecular weight (according to SEC measurements) among all other samples. The removal of galactose side groups makes XG less hydrophilic and this facilitates a more homogenous reaction in the organic solvent.

Finally, a change in monomer/free initiator ratio from 1:25 to 1:50 resulted in not only a higher viscosity of the reaction mixture, but also higher molecular weights for the formed PLLA, indicating that this type of reaction benefits from a rather high ratio of XG/L-lactide.

Immersion of the grafted substrates in water also demonstrated the efficiency of the grafting reaction. Native XG was completely soluble in water. However, the presence of grafted hydrophobic chains (PLLA) made it insoluble in water, as can be seen in Fig. 3.

Table 1
Characterization of free PLLA formed during the grafting of PLLA from XG.

Substrate	Target DP	m_{XG}/m_{LLA}	Conversion	Theoretical M_w (g/mol)	M_n NMR (g/mol)[a]	M_n SEC (g/mol)	PDI[b]
Native XG	DP150	1/25	83%	21,600	9100	8100	1.5
Native XG[c]	DP300	1/50	93%	43,200	13,000	22,000	1.5
Modified XG[d]	DP300	1/50	95%	43,200	12,200	24,300	1.4

[a] Obtained by ^{1}H NMR, using signals at 4.3 ppm ($CH(CH_3)O$, end group) and 5.2 ppm ($CH(CH_3)O$, repeating unit).
[b] Polydispersity index, obtained from SEC.
[c] This line corresponds to an average of two identical reactions.
[d] Enzymatically modified XG.

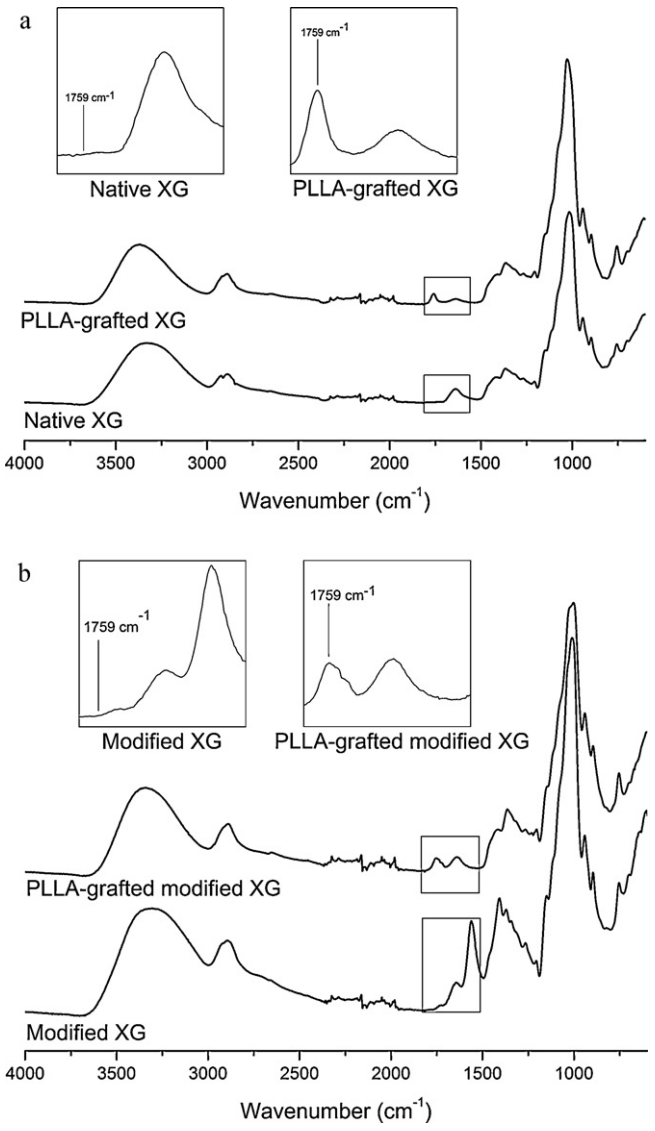

Fig. 4. FTIR spectra of native (top) and modified (bottom) XG substrates, together with their PLLA-grafted versions.

FTIR spectroscopy was used to characterize the XG substrates and their grafted PLLA chains. FTIR spectra for grafted and non-grafted native and modified XG samples are shown in Fig. 4. The grafting of PLLA chains from the XG substrates (native or enzymatically modified) can be seen in the FTIR spectra through the appearance of a new peak in the carbonyl region, around 1759 cm^{-1}.

3.2. Thermal analysis

The DSC thermograms for native XG, for pure PLLA obtained from the reaction mixture, and for the PLLA-grafted native XG are presented in Figs. 5–7, respectively. Since XG is amorphous, no melting point can be observed. The glass transition temperature (T_g) is around 252 °C, followed by subsequent degradation of the material (from 280 °C). This fact was evidenced also by the final product, turning into a black carbonaceous mass in the crucible.

According to DSC measurements, the characteristic temperatures of PLLA resulting from the reaction mixture were the following: the glass transition was 53 °C, the crystallization temperature was 91 °C and the melting point was 171 °C, which is consistent with values reported in the literature (Garlotta, 2001).

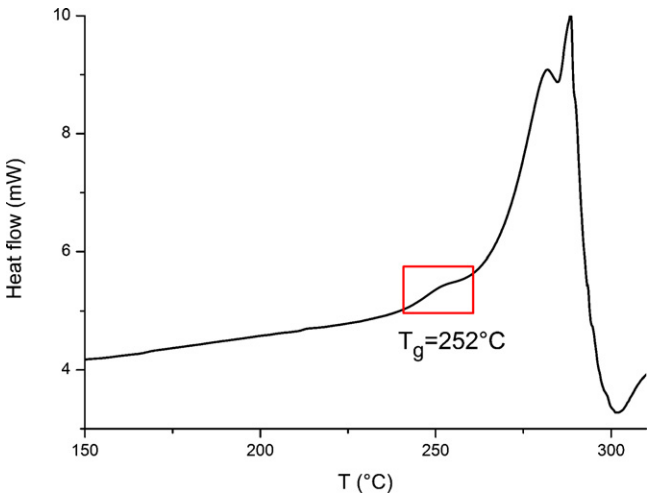

Fig. 5. DSC thermogram for native XG.

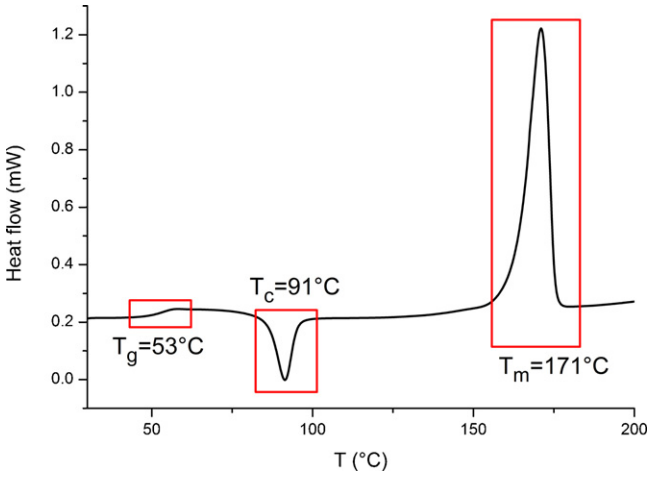

Fig. 6. DSC thermogram for free PLLA.

DSC results showed that the glass transition temperature of PLLA-grafted XG is significantly reduced compared with neat XG; the T_g of PLLA-grafted XG is 216 °C whereas it is 252 °C for native XG. This clearly demonstrates that PLLA chains were grafted from XG,

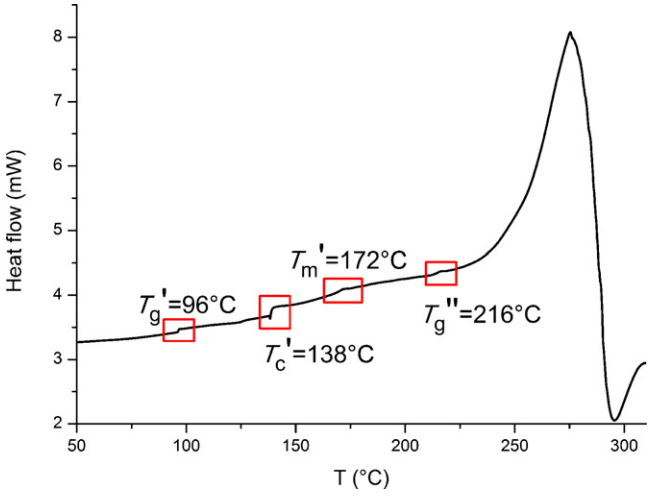

Fig. 7. DSC thermogram for PLLA-grafted XG from native substrate, where T'_g, T'_c, T'_m are respectively T_g, T_c and T_m of the grafted PLLA and T''_g the T_g of the PLLA-grafted native XG.

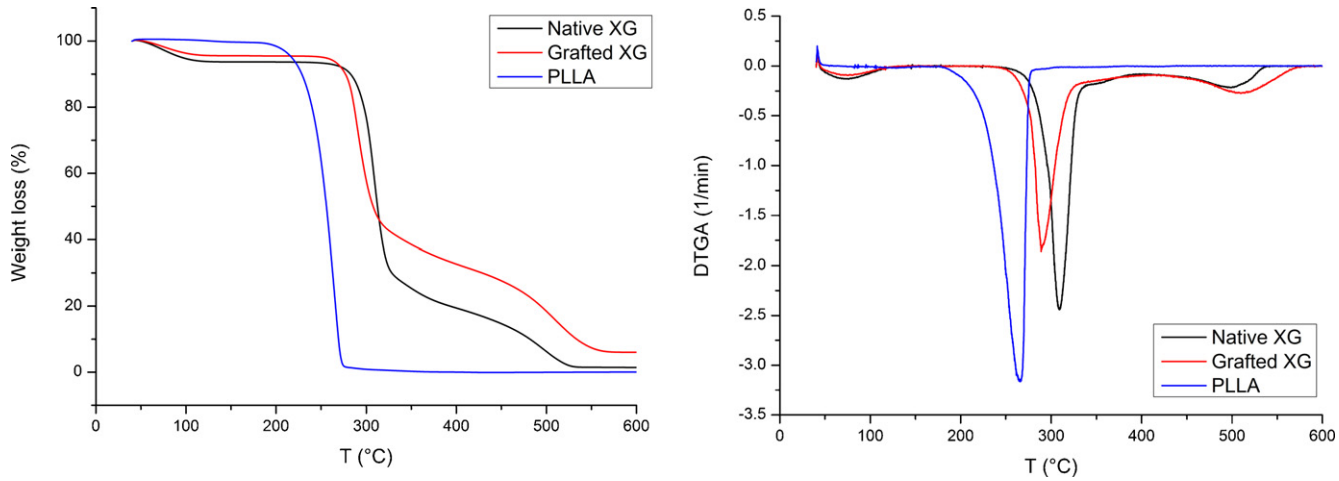

Fig. 8. TGA (left) and first derivative (right) results for native XG, grafted XG and free PLLA.

and that the grafting density was enough to enhance the mobility of XG chains, resulting in decreased T_g. This observation was consistent with previous results (from SEC and FTIR) and further proves that the grafting reaction was successful. In addition to this, the glass transition (T'_g), the crystallization (T'_c) and the melting (T'_m) temperatures of the grafted PLLA are visible in Fig. 7. The melting point was the same as that for non-grafted PLLA. However, the glass transition, as well as the crystallization temperature, was significantly increased by the grafting. The main reason why these temperatures are increased is that grafted PLLA is covalently attached and the chain mobility is restricted compared with pure PLLA.

Thermal analysis via TGA was used to study the degradation behavior of grafted XG compared with the unmodified XG and free PLLA. The thermogram and its first derivative (DTGA) are shown in Fig. 8 for native XG, grafted XG and free PLLA from the grafting reaction. As can be seen, the curves of grafted XG were between PLLA and native XG in the degradation temperature region (around 300 °C). This once again confirms that PLLA chains were grafted to XG, resulting in a decrease in the degradation temperature.

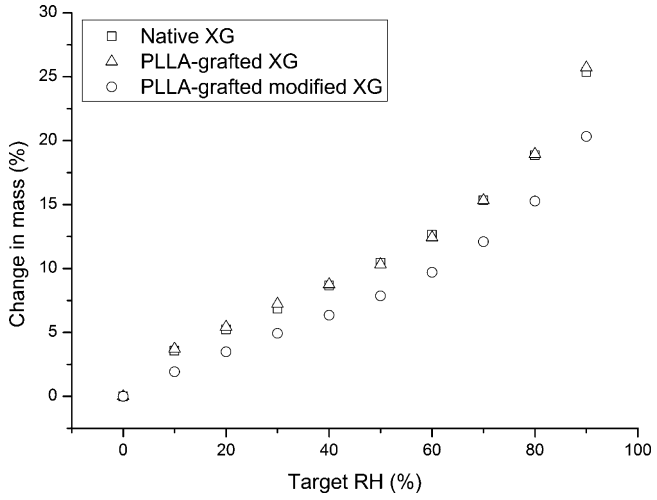

Fig. 9. Moisture sorption isotherms for native XG, PLLA-grafted native XG and PLLA-grafted enzymatically modified XG.

3.3. Moisture uptake

DVS analysis was carried out to see if the grafting of hydrophobic PLLA chains leads to a decrease in the water uptake of XG. Fig. 9 shows the moisture sorption isotherms for native XG as well as for PLLA-grafted XG and PLLA-grafted modified XG.

No differences were observed between native XG and grafted XG in terms of moisture uptake. On the other hand, grafting of PLLA chains to modified XG (with lesser number of galactose side groups) resulted in a relative decrease in moisture content of around 30% (in the practically useful RH of 30–80%) as compared to the native XG. It was demonstrated in a previous study that enzymatic treatment and the removal of around 30% of galactose side groups did not change water sorption properties of XG (Kochumalayil et al., 2010). The difference that can be observed here is then exclusively due to the grafting of hydrophobic PLLA chains from the surface of XG. The grafting appeared to be more efficient (higher grafting density and chain length) for the modified XG, causing decreased moisture uptake.

4. Conclusions

The chemical modification of high molar mass xyloglucan (XG) with poly(L-lactic acid) was investigated in this study. PLLA chains were successfully grafted from XG via ring-opening polymerization of L-lactide. The presence of moisture in the reaction system, the nature of the substrate and the ratio of substrate/monomer are key parameters in accomplishing good grafting efficiency; minimization of residual water, enzymatic removal of galactose residues from XG, and increase in the substrate/monomer ratio improve the efficiency of the grafting, i.e., increase the length of the grafted chains (on the assumption that the grafted chains follow the same trend as the free benzyl alcohol-initiated chains). Grafting with PLLA decreased the glass transition temperature of XG from 252 °C to 216 °C. Finally, the grafting of hydrophobic chains on the surface of the hydrophilic XG led to changed interaction with water: the water uptake of PLLA-grafted XG was at best reduced about 30% (in the region of RH from 30% to 80%) compared to native XG, and the water solubility was also significantly decreased.

PLLA-grafted XG is a new high molar mass compatibilizer for potential use in cellulose fiber-reinforced PLLA composite applications. XG has strong affinity for cellulose and the grafted PLLA may form physical entanglements with the PLLA matrix. The concept

may be useful also for other polymer matrices used with cellulose fibers or nanoparticles.

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