

論文の内容の要旨

生物材料科学専攻

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論文題目 Syntheses and characterization of xylan esters and their applications  
(キシランエステル誘導体の合成と性質およびその応用に関する研究)

Plant biomass has been the most important source of renewable polysaccharides which includes starch, cellulose and hemicelluloses. The major hemicellulose mostly found in plants is xylan. This polysaccharide has a backbone consisting of  $\beta$ -(1-4) linked xylose units. Recently, xylan gains increasing importance for the basis of new biopolymeric materials. In this research, xylan was chemically modified by esterification (Fig 1).

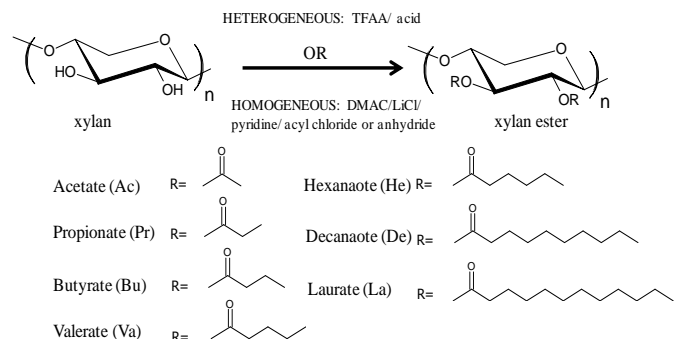


Fig 1. Esterification of xylan.

The products were characterized based on their structure, solubility, thermal and mechanical properties. The application of these xylan esters as bio-based nucleating agents for PLA was of primary interest. Film and nanofiber formation of the xylan esters were considered as well.

Xylan was first extracted from eucalyptus hardwood pulp by alkaline treatment with different concentrations of NaOH solutions. Higher yield was obtained with higher alkaline solution. Structure elucidation of the extracted xylan was done by NMR (Nuclear Magnetic Resonance). Results revealed that the extracted xylan did not contain acetyl groups and other sugars aside from xylose. This confirms that the extracted xylan was a homoxylan. Based on thermogravimetric analysis (TGA) the xylans extracted with higher alkaline concentrations had better thermal stability. This is possibly due to the extraction of higher

molecular weight xylan. In the preparation of xylan esters, xylan extracted with 10% NaOH was used. This yielded 6-8% xylan. Although higher yield can be obtained at higher alkaline concentration, it required a significant amount of acid for neutralization. This may not be practical for industrial application considering that the yield was not significantly higher.

Acetylation of xylan was carried out by homogeneous reaction in DMAc/LiCl system. The reaction was done at different reaction times in order to monitor the DS. Fully acetylated xylan (DS=2.0) was achieved within 6 h. Results revealed almost the same DS values at C-2 and C-3 positions of xylan acetate (XylAc) indicating the non-selectivity of the reaction. In the  $^1\text{H-NMR}$  spectrum of XylAc (Fig 2),

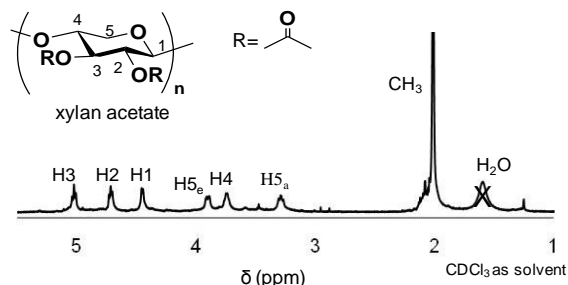


Fig 2.  $^1\text{H-NMR}$  spectrum of xylan acetate (XylAc).

the signal at  $\delta$  2.0 ppm corresponds to the methyl protons. This indicates successful acetylation of xylan. Meanwhile, the signals between  $\delta$  3.3 to 5.0 ppm are assigned to the ring protons of XylAc. Changes in the structure of xylan brought about by acetylation lead to an improvement in its thermal stability. XylAc with higher DS had better thermal stability. Likewise, the solubility of xylan in  $\text{CHCl}_3$  also increased. Perpropionylation of partially substituted xylan further increased its thermal stability and solubility in  $\text{CHCl}_3$ . DSC and WAXD results of xylan acetate propionate suggest pseudo-crystallization of the side chains. The mechanical properties of xylan acetate propionate films were dependent on the DS. The xylan acetate propionate film having a lower  $\text{DS}_{\text{Ac}}$  exhibited a higher tensile strength and elongation at break.

Synthesis of low molecular weight (LMW) and high molecular weight (HMW) xylan esters having varying alkyl chain lengths (C2-C12) were done by heterogeneous (TFFA/acid) and homogeneous (DMAc/LiCl) reactions, respectively. The structural features of the xylan esters (DS=2.0) were elucidated by NMR analysis. Based on TGA, the thermal stability of xylan increased after esterification. Xylan esters with longer alkyl chains had higher decomposition temperatures. The solubility of xylan in  $\text{CHCl}_3$  also increased after esterification.

The ability of the xylan esters to form films was dependent on their molecular weight and solubility in  $\text{CHCl}_3$ . LMW xylan esters with alkyl chains containing  $n \geq 6$  carbons (XylHe, XylDe and XylLa) were able to form continuous films. In the case of the HMW xylan esters, films were formed when the alkyl chains contained  $n \geq 3$  (XylBu, XylVa, XylHe, XylDe and XylLa). Tensile test done on HMW xylan ester films showed that the tensile strength and Young's modulus of xylan esters decreased with increase in alkyl chain length while the elongation at break increases (Fig 3). From the contact angle measurements, the hydrophobicity of the xylan ester films increased with increase in alkyl chain length. The surface contact angle of xylan ester films with longer alkyl chains ranged from 95

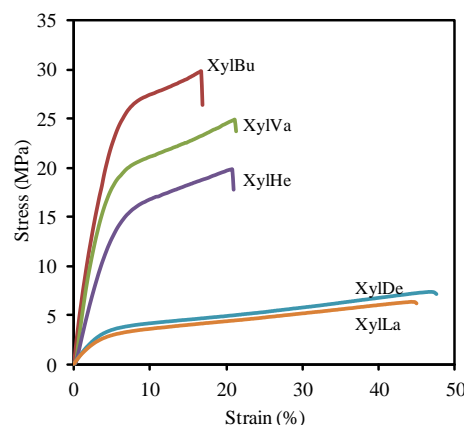


Fig 3. Stress-strain curves of HMW xylan ester films.

to 99°. X-ray diffractograms of the xylan esters films show the presence peaks in the low angle region suggesting the presence of side chain crystals (Fig 4). However, the results from DSC measurement did not reveal any side chain melting (Fig 5). This indicates that only pseudo crystals were formed. Likewise, glass  $T_g$  was also not observed for all samples even when faster heating rate was employed during DSC analysis. This observation is in good agreement with the results obtained from DMA (Dynamic Mechanical Analysis) where a drop in storage modulus was not seen in the curve. Electrospinning of solutions of HMW xylan esters in HFIP produced beaded fibers. XylAc, XylPr, XylBu, XylVa and XylHe can be electrospun into nanofibers (Fig 6). However, XylDe and XylLa were not soluble in HFIP.

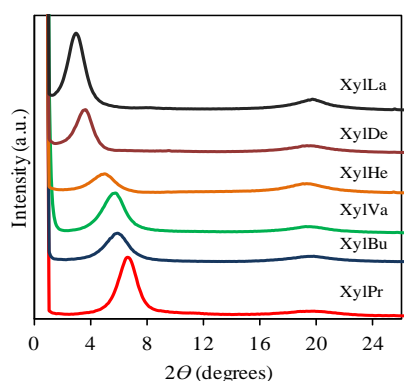


Fig 4. X-ray diffractograms of HMW xylan ester films.

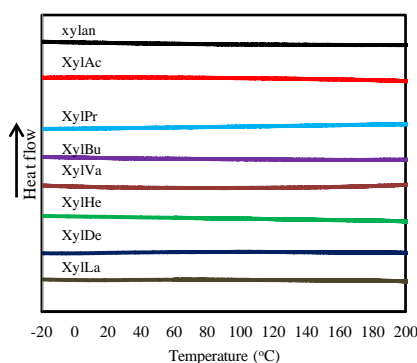


Fig 5. DSC traces of xylan esters in the 2<sup>nd</sup> heating scan.

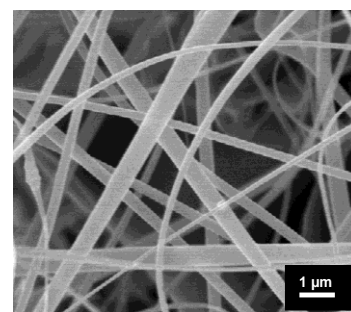


Fig 6. HMW XylAc nanofibers.

One of the primary interests of this research is the application of xylan esters as bio-based nucleating agents for PLA (PLLA and PDLA). The effect low molecular weight (LMW) and high molecular weight (HMW) xylan esters (C2-C12) on the crystallization behavior of PLLA were investigated. Non-isothermal crystallization study on PLLA and PLLA blends containing LMW and HMW xylan esters were studied. In both cases, only XylPr and XylBu were effective in lowering the crystallization temperature ( $T_c$ ) of PLLA. Other xylan esters with longer alkyl chains showed an inhibitory effect on the crystallization of PLLA. Figure 7 shows the endotherms of PLLA blends containing 1% LMW xylan esters. Blending of LMW XylPr and LMW XylBu decreased the  $T_c$  of PLLA from 126 to 95 and 97 °C, respectively. Similar results were obtained when HMW xylan esters were used. Different concentrations of LMW XylPr and LMW XylBu in the PLLA blends produced comparable results. Melt crystallization study revealed that these xylan esters can enhance the crystallization of PLLA even at faster cooling rate. In addition, LMW XylPr can act as better nucleator than LMW XylBu for PLLA. It is speculated that the aggregation of these xylan esters acts as nucleating centers and thus enhancing the crystallization of PLLA.

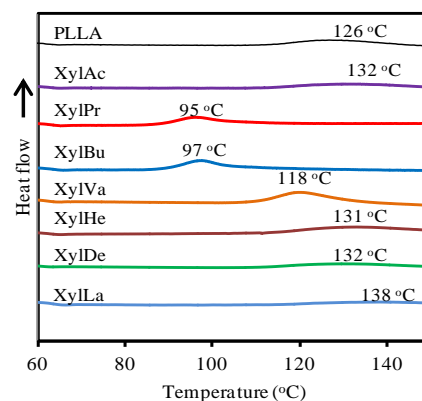


Fig 7. Endotherms of PLLA and its blends containing 1% LMW xylan esters.

Isothermal crystallization study show that the half time crystallization ( $t_{1/2}$ ) of PLLA decreased when blended with LMW XylPr and LMW XylBu (Fig 8). The  $t_{1/2}$  of PLLA, 1% LMW XylPr/PLLA and 1% LMW XylBu/PLLA isothermally crystallized at 130 °C were 13.6, 3.1 and 5.7 min, respectively. POM images reveal that the spherulites of PLLA blends containing the xylan esters were smaller and denser compared to PLLA (Fig 9). These results confirm the increase in the number of nucleating centers in the presence of the xylan esters. WAXD results showed that the crystallinity ( $X_c$ ) of the PLLA blend films was higher compared to neat PLLA. When PLLA was annealed for 10 min at 100 °C, the  $X_c$  was only 32%. However, in the presence of the xylan esters, the  $X_c$  almost reached 50%. Although the PLLA blends had higher  $X_c$ , the films were more optically clear than neat PLLA based on the haze measurements (Fig 10). This is attributed to the presence of smaller spherulites in PLLA blends. In addition, the PLLA blend films had lower thermal expansion compared to PLLA based on TMA; hence, more resistant to heat deformation. Similar results were also obtained with PDLA blends.

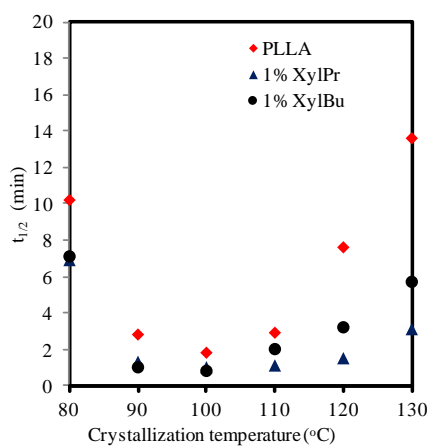


Fig 8. Plots of  $t_{1/2}$  vs  $T_c$  of PLLA and its blends containing LMW esters.

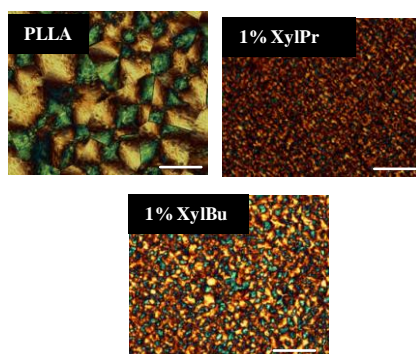


Fig 9. Spherulite images of PLLA and its blends containing LMW esters isothermally crystallized at 130 °C.

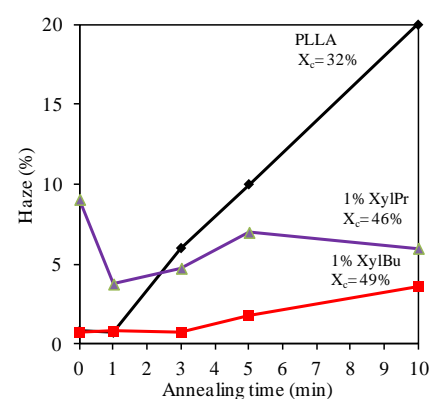


Fig 10. Haze as a function of time of PLLA and its blend containing LMW esters annealed at 100 °C

The effectiveness of XylPr and XylBu as nucleators for PLA could be a result of the aggregation of these xylan esters. These aggregates act as nucleating centers which initiates the crystallization of PLA. It is hypothesized that the sum of the  $d$ -spacings of these aggregates is approximately the same with one of the lattice parameters of PLA.