

SYNTHESIS AND CHARACTERIZATION OF XYLAN AND GLUCOMANNAN ESTER DERIVATIVES AND THEIR CRYSTALLIZATION EFFECTS FOR POLY(LACTIC ACID)

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Xylan is the most abundant hemicellulose with mainly beta-(1→4) linked xylose and it gains increasing importance for the basis of new biopolymeric materials. On the other hand, glucomannan is one of natural polysaccharides and can be isolated from konjak. In this paper, we synthesized xylan and glucomannan ester derivatives and investigated thermal and mechanical properties of solvent-cast and melt-pressed films of these ester derivatives. Furthermore, in the case of xylan ester derivatives, we demonstrated a possibility of xylan esters as bio-based nucleating agents for PLLA and PDLA.

Xylan was first extracted from eucalyptus hardwood pulp by alkaline treatment with different concentrations of NaOH solutions. Xylan ester derivatives were synthesized as shown in Figure 1.

Xylan was esterified with different acyl groups and products were analyzed by NMR, DSC, TG, GPC and WAXD analyses. Films can be processed resulted to an improvement in thermal stability.¹

The xylan esters were screened for their effect on the crystallization

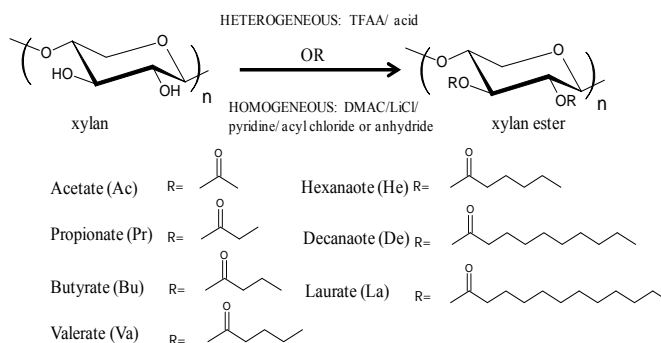


Fig 1. Esterification of xylan.

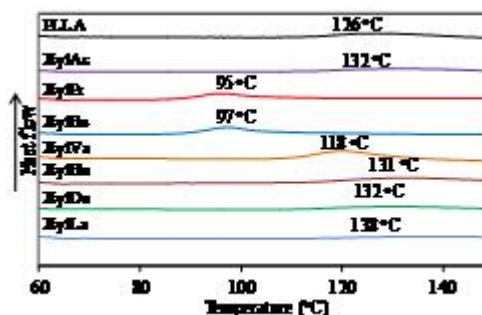


Fig 2. Endotherms of PLLA and its blends containing 1% xylan esters.

behavior of PLLA. Figure 2 shows the DSC traces of PLLA and PLLA blend films with 1% xylan esters. XylPr and XylBu showed an excellent effect on the crystallization behavior of PLLA. The exothermic peak, which is attributed to the crystallization of PLLA, was shifted to a lower temperature with the addition of these xylan esters.

Figure 3 presents the plots of $t_{1/2}$ values of the PLLA and PLLA blends at different T_c s. Results revealed that the $t_{1/2}$ is dependent on the T_c . In the case of PLLA, the rate of crystallization was fastest at 100 °C ($t_{1/2}$ = 1.8 min) and slowest at 130 °C ($t_{1/2}$ =13.6 min). The same trend was observed for the PLLA blends. The $t_{1/2}$ values of the PLLA blend with XylPr and with XylBu at 100 °C were 1.0 and 0.8 min, respectively. Based on these results, XylPr and XylBu are effective in enhancing the crystallization rate of PLLA during isothermal crystallization.

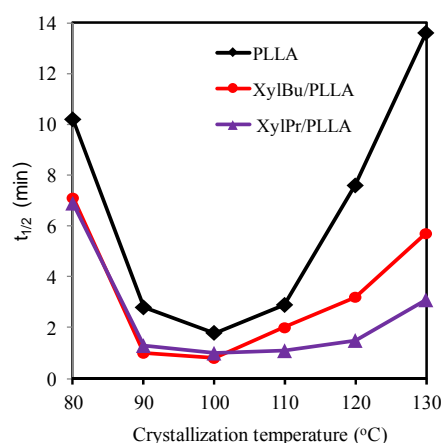


Figure 3. Plots of $t_{1/2}$ values and T_c s of PLLA and its blends with 1% xylan esters.

Spherulites of xylan ester/PLLA grown after isothermal crystallization were observed to be smaller and denser compared to that of PLLA. These results indicate that xylan propionate and xylan butylate act as excellent bio-based nucleating agents for PLLA.

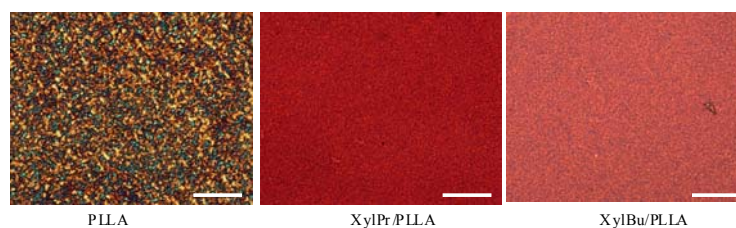


Figure 4. Spherulite images of PLLA and its blends isothermally grown at 100 °C (Scale bar= 100 μ m)

In the case of glucomannan ester derivatives, tensile strength and elongation at break depend on acyl groups. Glucomannan esters have not T_m as same as xylan esters, however, melt-pressed films could be processed by hot-pressing at the temperature above T_g .

References:

1. Fundador N., Enomoto-Rogers Y., Takemura A., Iwata T., Carbohydr. Polym. **87**: 170-176, 2012.