Hemicellulose based polylactide copolymers, synthesis and characterization

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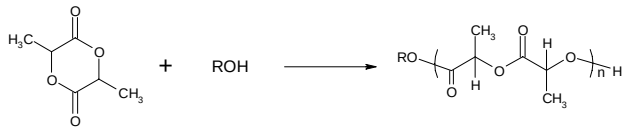
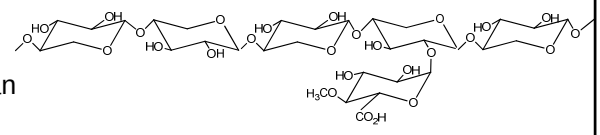
Background

- Lactide
  - Dimer of lactic acid. Produced by fermentation of carbohydrates
  - Polymerized by ring opening polymerisation (ROP)
- Grafting and blends with polysaccharides
  - Biodegradable
  - Introduce thermoplastic qualities
  - Biomimetic scaffolds, sutures, composite materials etc..



- Aim: PLA-g-xylan
  - Matrix material in cellulose fiber reinforced composites?

Xylan starting material



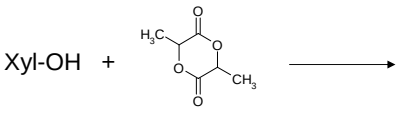
- 4-*O*-methylglucoronoxylan
  - Isolated from birch wood kraft cooking liquor
  - Bleached with sodium chlorite to remove lignin impurities

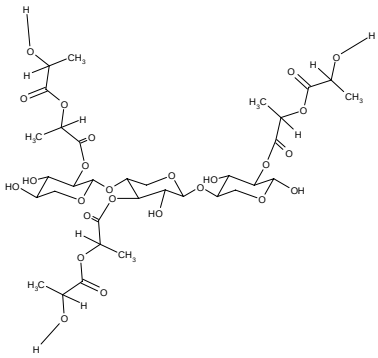
Birch black liquor xylan before and after delignification

	Xylan (Rel. wt%)	Lignin (Rel. wt%)	Mw (g/mol)	PD (Mw/Mn)
BW Xylan	**83.6**	**11.3**	**12,000**	**1.2**
B.BW Xylan	**97.3**	**0.8**	**13,000**	**1.2**

Grafting reaction with lactide

- Xylan OH-groups –initiators for ROP of lactide



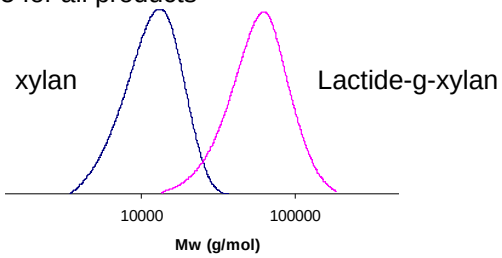


- Catalyst: Sn(II)oct$_2$
- Temp: 95°C
- Time: 22 hrs
- Lactide/Xylan molar feed ratio: 2-15

Chemical Characterization

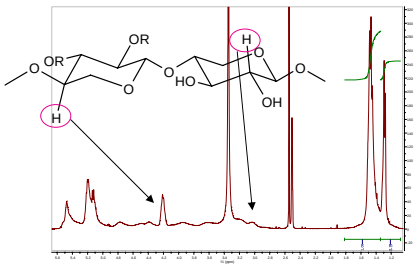
- Low lactide feed ratio – water soluble product
- Higher lactide feed ratio –water insoluble products

- Size exclusion chromatography
  - Mw increased with higher feed ratios from 13,000 to 60,000
  - Polydispersity around 1.5 for all products

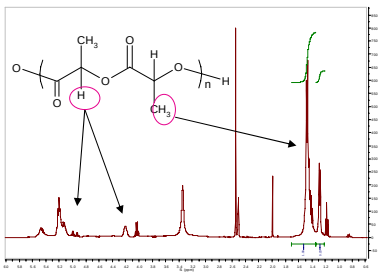


Chemical Characterization

- ^{1}H NMR
  - Increased feed ratio – longer lactide chains
  - 60-80% conversion of xylan units



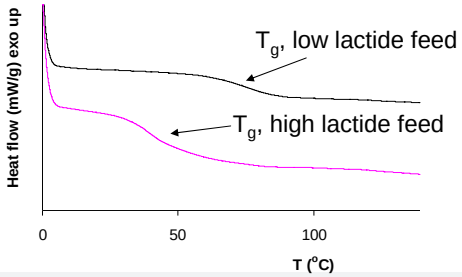
^{1}H NMR DP_{La} = 2



^{1}H NMR DP_{La} = 5

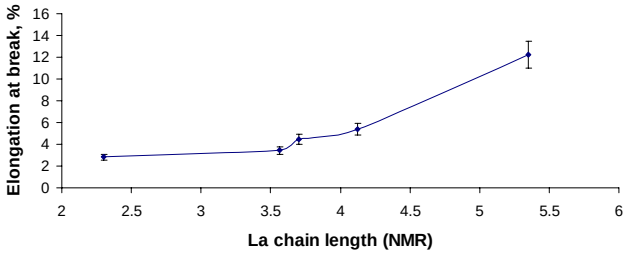
Thermal Properties

- TGA –measurement of Decomposition Temperature, T_d (onset)
  - Xylan: T_d=250°C
  - Products: T_d=260-310°C
- DSC –measurement of Glass Transition Temperature , T_g
  - T_g decreased with increased lactide chain length



Mechanical Properties

- Increased lactide chain length
  - Decreased Young's modulus from 3.4 to 1.3 GPa
  - Decreased Stress at break from 50 to 20 MPa
  - Increased Elongation at break



Conclusions

- Lactide grafted on birch wood xylan
- Higher lactide/xylan feed ratios resulted in longer lactide chains
- Narrow molecular weight distributions
- Increased flexibility and decreased T_g

Thank you for listening!

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