Renewable Bio-composites for Automotive Applications

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Research and
Advanced Engineering

Outline

- Background
- PLA composites project goals and benefits
- Technical challenges
- Progress and results to date
- Next steps
- Acknowledgements

Ford's Stance on Sustainability

'Consumers will insist on doing business with companies they can trust, companies that do the right things environmentally and ethically, as well as economically. To fully meet the expectations of those consumers, companies are going to have to address the concerns of the society'

Bill Ford
Executive Chairman

Current Uses of PLA

- Automotive
  - Toyota:
    - floor mats, compression molded spare tire cover
  - Mitsubishi
    - Prototype floor mats

courtesy Toyota

- Non-automotive
  - Clothing
  - Linens
  - Blow molded applications for food packaging
  - Film applications for shrink wrap and bags

courtesy NatureWorks

Injection molded end use applications yet to be fully commercialized!

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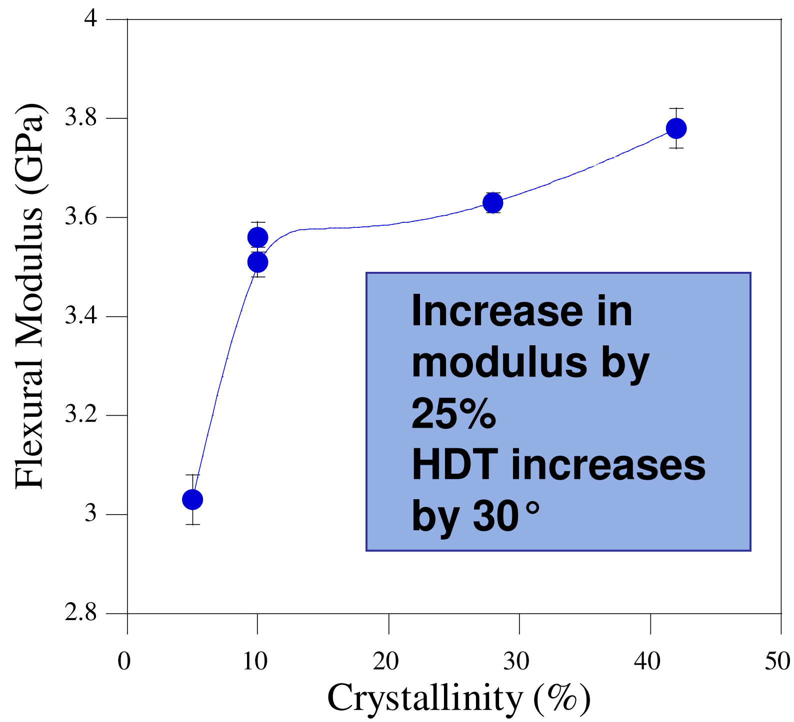
Injection Molded Bio-composites

- Goals
  - Increase crystallinity and performance with the addition of natural fillers
  - Understand the effects of thermo-mechanical processing on PLA degradation
  - Achieve balance between durability and degradability (end-of-life)

- Benefits
  - Made from renewable resources
  - Possible cost advantage over petroleum based products
  - Compostable

PLA Performance Dependence on Crystallinity

- For neat PLA, a crystalline sample has improved flexural and heat deflection properties
- PLA has slow crystallization rate
  - Favors amorphous structure vs. the desired crystalline structure
  - Longer cycle time during the injection molding process



Neat PLA crystallization rate is too slow – Need nucleating agents

Addition of Fillers

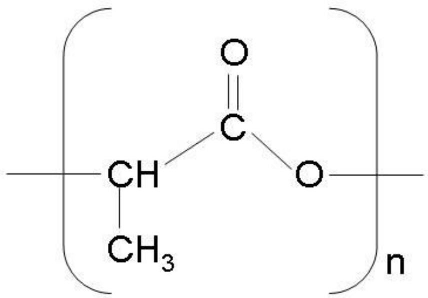
- Benefits of adding natural fillers
  - Act as a nucleating agent
    - Improve crystallization rate
    - Increase overall crystallinity
  - Act as a reinforcement
    - Improve overall performance
  - Create a truly "green" composite
    - Will not negatively affect the compostability of the composite

Technical Challenges to Overcome

- Improvements in mechanical properties to meet automotive material specifications
  - Flexural properties
  - Impact strength
  - Heat deflection temperature
- Avoid/ limit degradation during processing

Materials

- Materials
  - Nature Works® PLA – injection molding
  - Various fillers
    - (2-10% loading levels)



The chemical repeat unit of PLA

- Natural fillers
  - Soy flour
    - 70 protein dispersibility index (PDI) – minimal heat treatment
  - Purified cellulose powder
  - Organically modified nanoclay – Nanocor I30P
  - Talc

Soy has been part of Ford Motor Company's history

2003

Model U concept car – soy based seating foam & polyester resin that is reinforced with fiberglass used to make the tailgate

2007

Ford Research developing soy reinforced plastics, including rubbers

1940

Henry Ford demonstrating the impact strength of a soy flour composite decklid

2006

Ford Research developed soy foam that passes automotive standards

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Soy Flour Partnerships

- United Soybean Board
  - Grant given to Ford to work on soy meal and soy flour reinforced plastics
- CHS Oilseed Processing
  - Provided soy flour materials

Advantages of Soy Flour

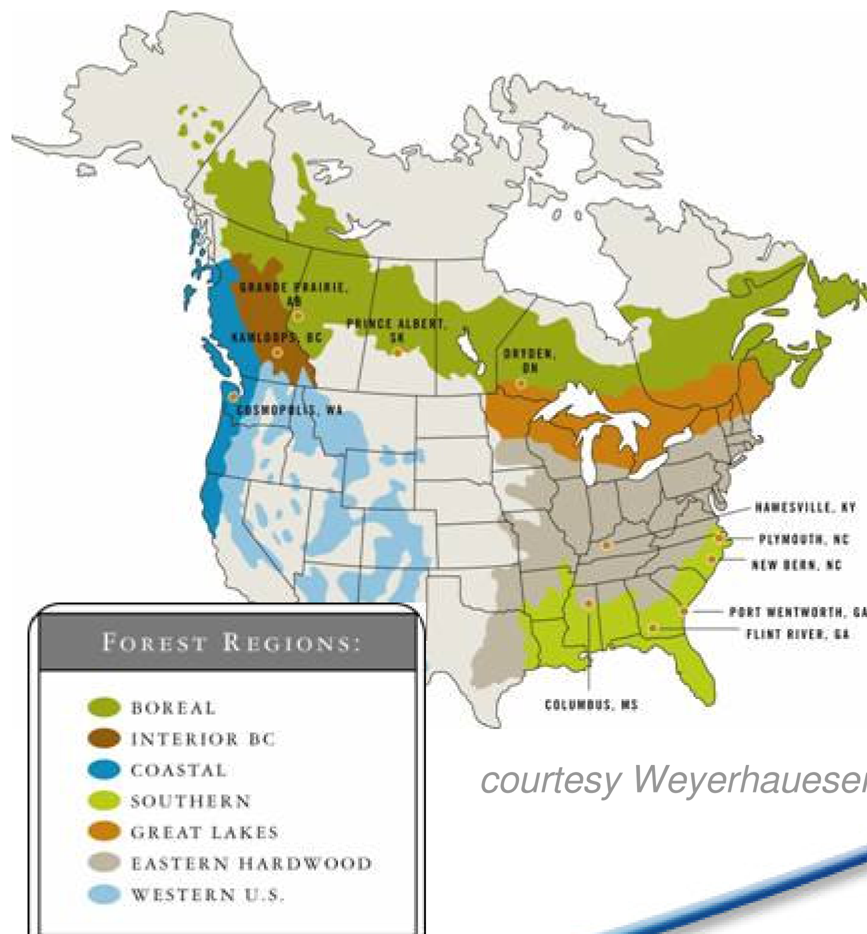
- Renewable/sustainable
- Soy meal and soy flour are bi-products of bio-diesel
- Anticipate greater production levels of soybean meal as bio-diesel production increases
  - 1999: U.S. consumed 0.5 million gallons bio-diesel*
  - 2004: U.S. consumed 30 million gallons bio-diesel*
- 2005 U.S. soybean meal production was ~40 million tons *
- Inexpensive – continue to decrease in cost

* Reference www.soystats.com

Cellulose Fiber

Each Tree Species Provides a Unique Set of Fiber and Performance Properties

Forest Region	Cellulose Fiber Grade	Primary Species
Interior BC	Northern softwood	Douglas fir, White spruce & lodge pole pine
Boreal	Northern softwood	White & black spruce, & jack pine, Aspen
Eastern Hardwood	Southern hardwood	Oak, gum, & yellow poplar
Southern	Southern softwood	southern pines such as loblolly, long leaf, short leaf, & slash



courtesy Weyerhaueser

Advantages of Cellulose Fiber

- Renewable/sustainable
  - sustainable forestry practiced
- Density
  - cellulose: 1.1 g/cm^3
  - glass: 2.6 g/cm^3
  - talc: 2.75 g/cm^3
- Purified cellulose has high thermal stability
- Cost: 30 – 80 ¢/lb, depending on fiber form and processing required

Compounding Composites

- Compounded materials into master batches at ~20% filler loading
- Twin screw extrusion
  - Thermo co-rotating screws
- Post extrusion
  - Water bath
  - Pelletizer
- Injection molded at desired filler loading levels

Characterization

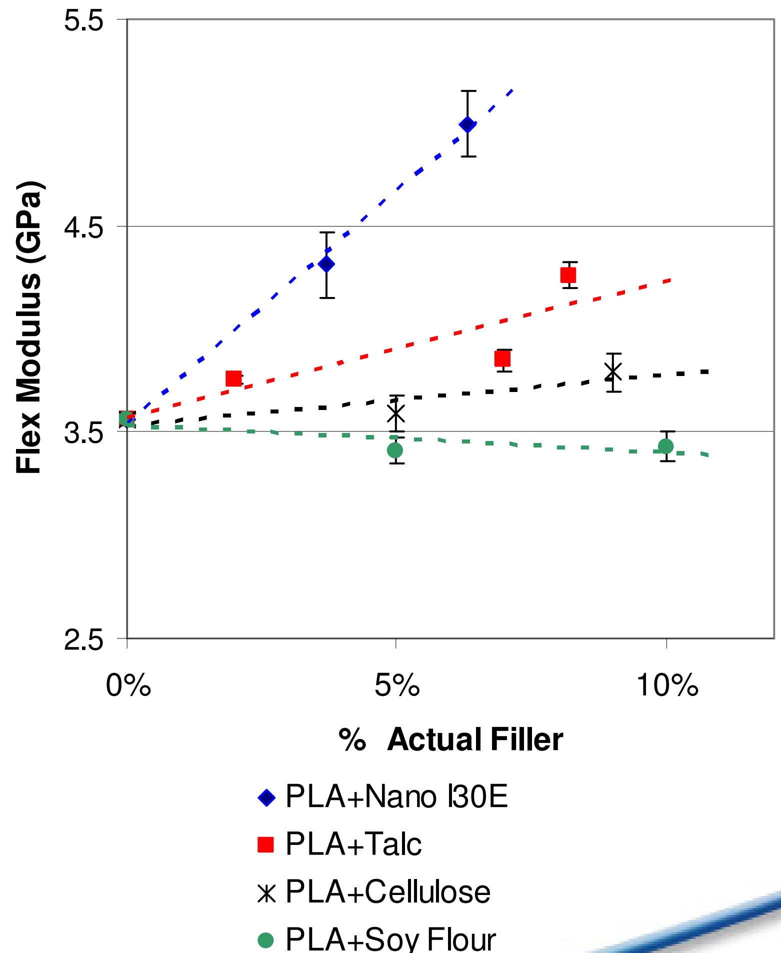
- Flexural testing
- Differential Scanning Calorimetry (DSC)
- Gel Permeation Chromatography (GPC)
- Thermo Gravimetric Analysis (TGA)

Results: Flexural Testing

- Quasi-static three-point bend testing
  - ASTM D-790 method
- Strain rate of 1mm/min with a 50mm span at room temperature
- Flex modulus and strength calculated from a single experiment

Results: Flexural Testing

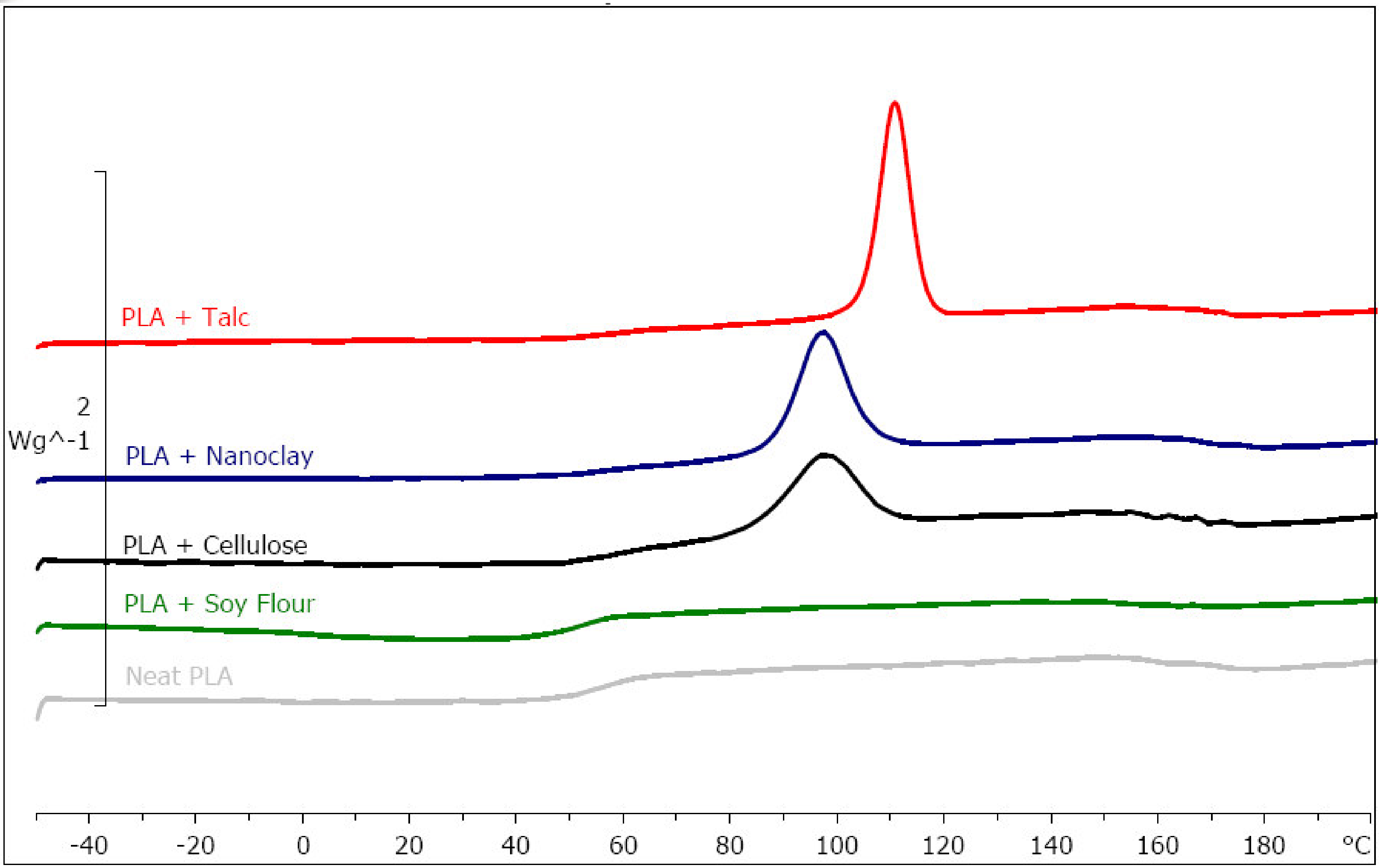
- Nanoclay the most effect reinforcing agent
- The use of soy flour as a filler for PLA does not show any significant reinforcing effects.



Results: Crystallization Behavior

- Differential scanning calorimetry (DSC)
- Crystallization temperature from the melt was determined during a cooling scan of 10℃/ min
- Samples taken from cross sections of injection molding bars
- Filler loading of ~10%

Results: Crystallization Behavior



Results: Crystallization Behavior

- Talc, nanoclay, and cellulose all seem to act as nucleating agents
- Talc samples crystallize much sooner and more quickly than the other samples – most effective nucleating agent
- Soy flour does not act as a nucleating agent

Filler	Crystallization Temp (°C)
Talc	111.1
Nanoclay	97.4
Cellulose	97.0
Soy Flour	n/a
None	n/a

Filler Comparisons

Filler	Renewable	Reinforcing	Nucleating
Soy Flour	Yes	No	No
Cellulose	Yes	Some	Yes
Clay	No	Yes	Yes
Talc	No	Yes	Yes

- Talc & clay better reinforcing agents
  - moduli higher than the moduli of cellulose and soy flour
- Better nucleating agents due to smaller particle sizes
  - nucleation efficiency increases due to increase of surface area (as expected with the reduction in particle size)

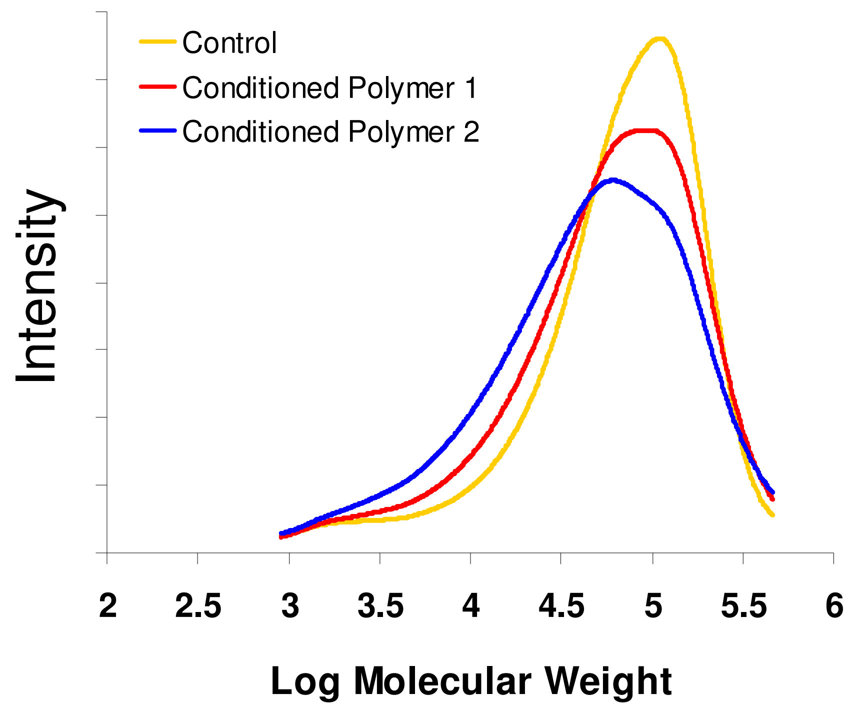
Filler Comparisons

- Poor interfacial adhesion between soy flour & cellulose particles and PLA polymer matrix
- Degradation during processing
  - Molecular weight decrease during processing due to hydrolysis
  - Cellulose and soy flour will not be as thermally stable as talc and clay
  - Investigate degradation
    - Molecular Weight Analysis of Neat PLA
    - TGA of fillers and PLA composites

Degradation: Molecular Weight

- Molecular weight monitored as a way to measure degradation
- Weight average (Mw) molecular weight of PLA measured using gel permeation chromatography (GPC)
- Molecular weights of PLA specimens were calculated from the PS molecular weights through the Mark-Houwink relationship:

$$[\eta] = kM^{a}$$

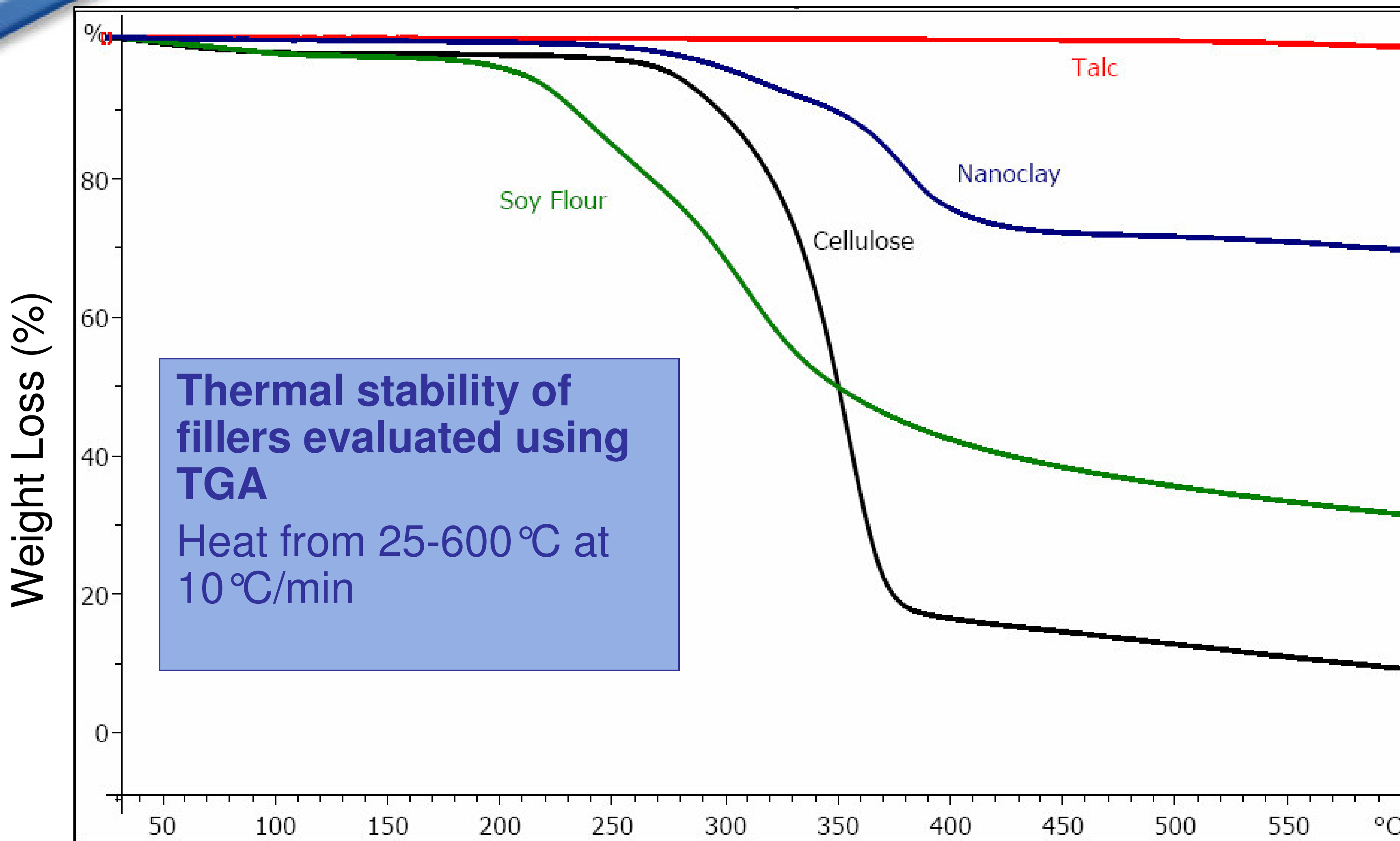


Effect of Processing on Neat PLA: Molecular Weight Evaluation

Samples	Residence time in barrel (min)	M_w (g/mol)	χ_c (%)
PLA Pellet	n/a	**$1.0*10^5 \pm 1\%$**	41%
Amorphous Injection Molded PLA	1.67	**$1.0*10^5 \pm 1\%$**	10%
Crystalline Injection Molded PLA	4.67	**$9.4*10^4 \pm 1\%$**	43%

- Slight dependence on molecular weight due to processing conditions (i.e. increased residence time in injection molding barrel)

TGA of Fillers



Thermal stability of fillers evaluated using TGA

Heat from 25-600℃ at 10℃/min

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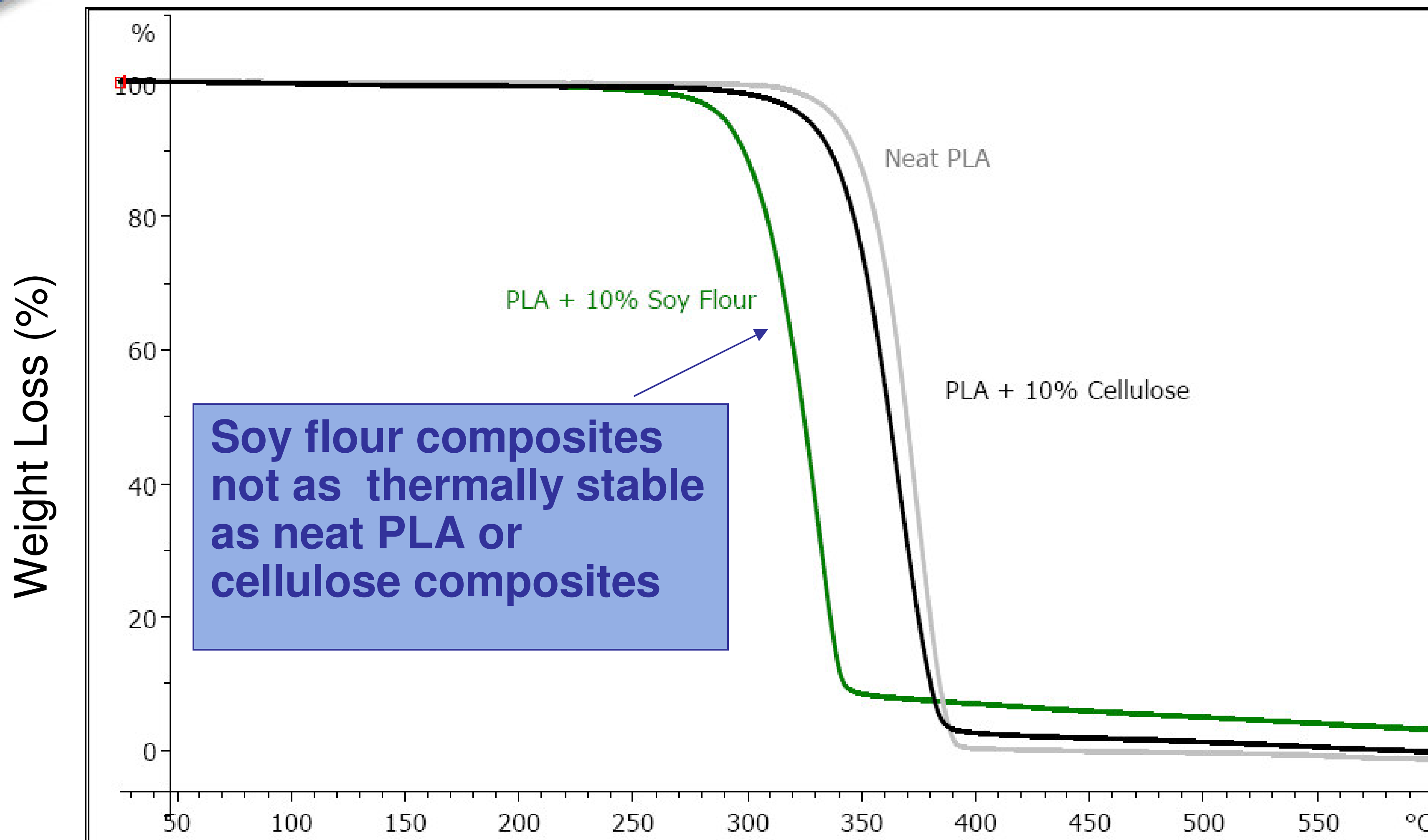
TGA of PLA Composites



Next Steps

- Coupling agents
  - Lysine diisocyanate (have had some success with PLA/ corn starch composites)
- Compatibilizers
- Evaluate other grades of soy flour with differing protein dispersibility indices and particle sizes
- Evaluate soy meal as potential filler
- Optimize processing conditions
- Durability/ conditioning experiments

Summary

- Choice of filler is critical to overall performance of composite
- Talc and nanoclay more effective reinforcing agents than cellulose or soy flour
- Talc, nanoclay and cellulose are more effective nucleating agents than soy flour
- Processing has minimal effect on degradation of neat PLA but could have a greater effect if thermally unstable fillers are used

Acknowledgements

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