NatureWorks LLC

Enhancing Performance of Biopolymers Through Polymer and Formulation Design

Jed Randall

NatureWorks LLC

BIOPLASTICS COMPOUNDING AND PROCESSING 2012

May 8-9, 2012, Miami, Florida

NatureWorks LLC

Our Mission

to be the global leader in producing a broad family of performance plastics from renewable resources, dedicated to meeting the world's needs today without compromising the earth's ability to meet the needs of tomorrow.

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Ingeo Technology Platforms

- ***8*** **series foam**
- ***7*** **series bottles - ISBM**
- ***6*** **series fibers & nonwovens**
- ***4*** **series films**
- ***3*** **series injection Molding**
- ***2*** **series thermoforming**
- **Lactide monomer**

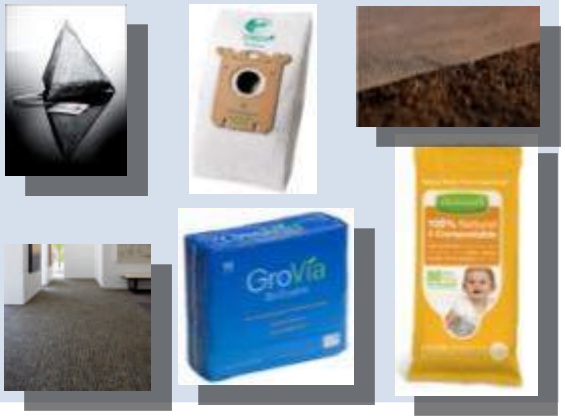
NatureWorks LLC Where we are in the Market

Rigids

Food Serviceware

Films

Nonwovens / Fibers



Durables

Lactides

INGEO™ LACTIDES

Bus. Dev.

Incubator

ingeo™

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Durable Material Choices

Amorphous Ingeo + Masterbatch

- Clear or Opaque
- Impact Modifier
- Tint
- High Bio Content
- Lower HDT

Ingeo + Petro Based Polymer Blend

- Clear w/ PMMA
  Opaque w/ PC or ABS
- High Impact & Heat
- Drop In Shrinkage
- Familiarity w/ 1 Component
- UL Flame Retardant Grades
- Moderate Bio Content

Crystalline Ingeo (cPLA)

- Opaque
- Tailored to Appl.
- Good Prop. Balance
- High Heat
- Moderate Shrink
- High Bio Content

Ingeo + Fiber Reinforcement

- Very High Strength
- High Heat
- Impact Improvement
- Long Glass Products
- High Bio Content

TEKNOR APEX
KA SUNO
Polyvel inc.
PolyOne
Plastics Color Corporation
ATP Engineering Plastics
TORAY Innovation by Chemistry
PolyOne
ARKEMA
TEKNOR APEX
ATP Engineering Plastics
PolyOne
kao Enriching lives, in harmony with nature.
ATP Engineering Plastics
TORAY Innovation by Chemistry

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New offerings and developments from NatureWorks LLC

- Engineered compounds for the food service industry
  - Based on new building blocks resulting from the BioAmber joint venture
  - Ingeo AW 240D for extrusion / thermoforming
  - Ingeo AW 300D for injection molding

- High Productivity, high heat performance grades
  - Family of high % L, highly crystalline Ingeo PLAs
  - Low and medium viscosity grades for injection molding and fibers
  - Available 2Q 2013
  - High viscosity for extrusion in development

- High flowing, easy sealing binder
  - Low viscosity, high % D amorphous Ingeo PLA in development

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NatureWorks Engineered Compounds Offering Expansion

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AmberWorks Biopolymer Solutions

A Joint Venture between BioAmber and NatureWorks

Facts

- JV between NatureWorks and BioAmber
- Founded in 2012
- Headquarters: Plymouth, Minnesota

Purpose

- Develop, Manufacture, and sell exclusively to NatureWorks compounded, bio-based performance polymer solutions

Business Model

- NatureWorks is the face of the JV to the market
- Compounded PBS/PLA Product Solutions will be Ingeo products, fueled by BioAmber bio succinic acid

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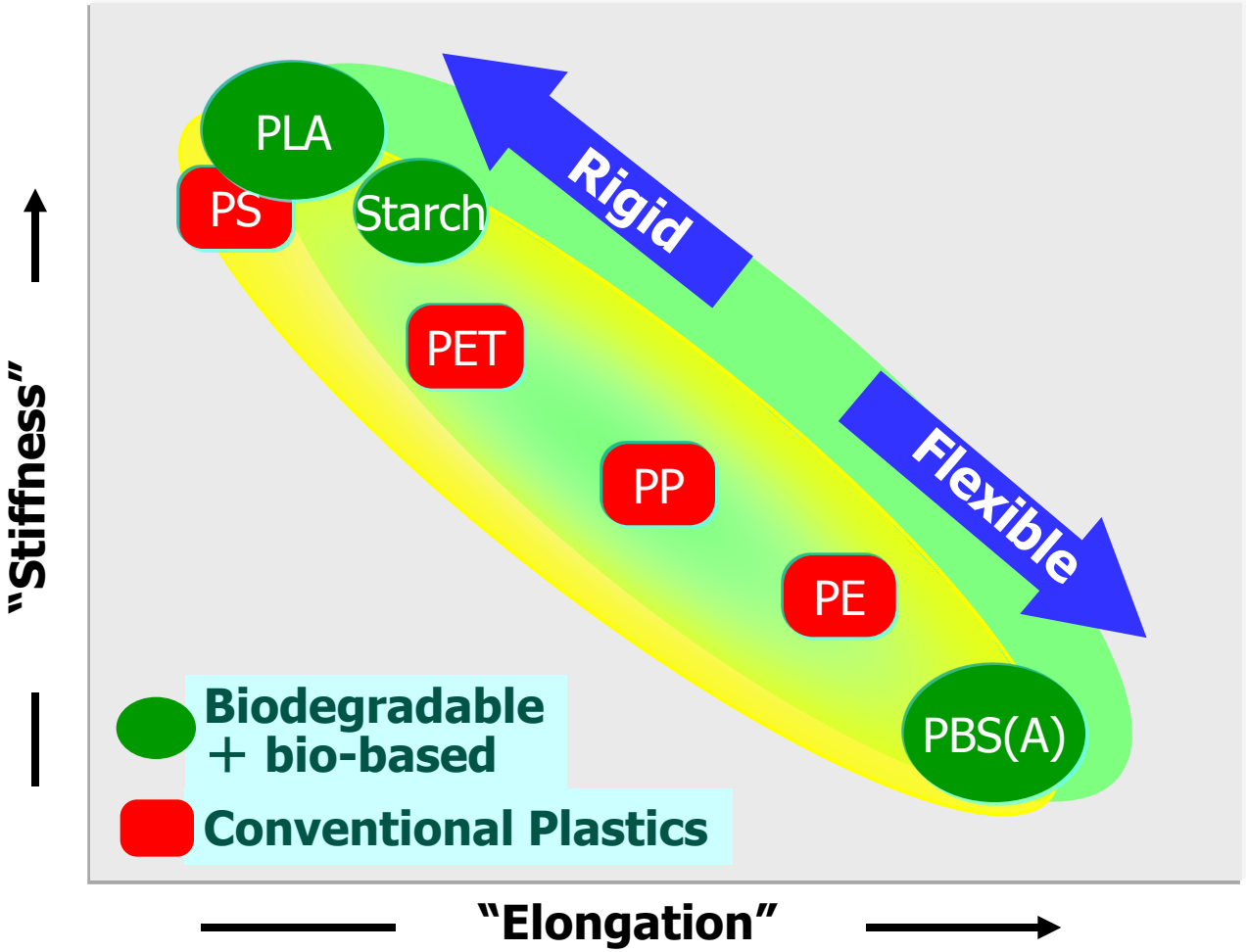
Broadening the addressable property window

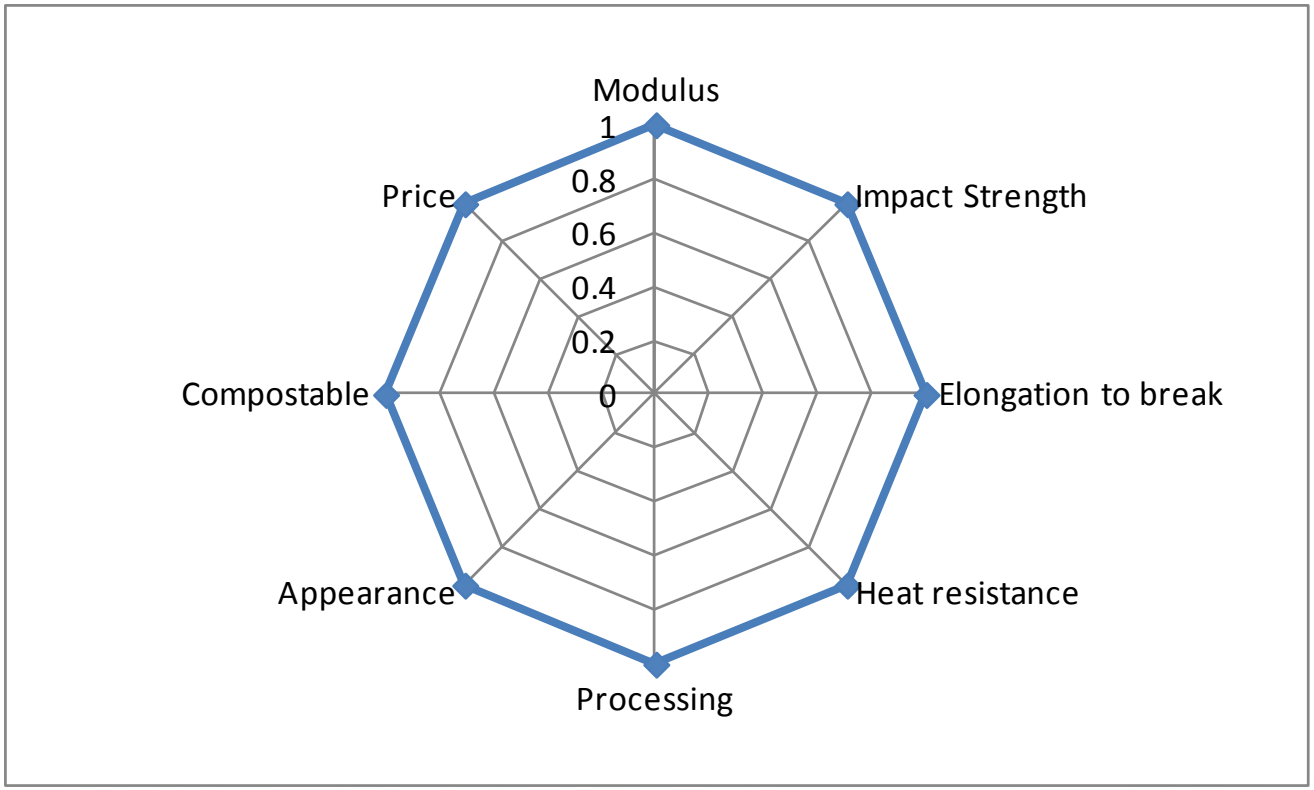
Performance Properties



Formulation design

Rigidity and elongation are the initial design criteria…

Optimizing the whole package for broad end use is the next step



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Available now for sampling: new developmental grades designed for food serviceware

- Thermoforming (Ingeo AW 240D)
- Injection Molding (Ingeo AW 300D)

- Expanded Ingeo property range
  - Flexibility
  - Heat resistance
  - Easy processing
  - Compostable – benefit for food waste diversion from landfills

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Ingeo AW 240D
Sheet and thermoforming typical properties

Typical Material & Application Properties (1)		
Physical Properties	**AW 240D**	**ASTM Method**
Specific Gravity	1.48	D792
MFR, g/10 min (190°C, 2.16kg)	6	D1238
Clarity	Opaque	
Mechanical Properties		
Flexural Modulus, kpsi (MPa)	239 (1650)	D790
Vicat Softening Point, °F (°C)	220 (105)	D1525
HDT @66 psi (0.455 MPa), °F (°C)	185 (85)	D648

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Ingeo AW 240D

Processing recommendation starting points, may need to be optimized

Processing Temperature Profile		
Melt Temperature	365ºF	185ºC
Feed Throat	113ºF	45ºC
Feed Temperature	340ºF	170ºC
Compression Section	350ºF	175ºC
Metering Section	365ºF	185ºC
Adapter	365ºF	185ºC
Die	365ºF	185ºC
Screw Speed	20-100 rpm	

Roll Temperature Profile	
Top roll	70 °F / 21 °C
Middle roll	120 °F / 49° C
Bottom roll	135 °F / 57 °C

Off-line Thermoforming

- A long preheat at 80-85°C
- Spreading rails 7 mm spread on 370 mm
- 3 shot oven, 24°C mold temperature and 13.7 cycles per minute
- Sheet temp. 105 - 110°C
- Plug assisted pressure with vacuum
- 72.5 psi (5 bar) for mold detail

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Ingeo AW 240D key benefits in thermoforms

- Polypropylene type feel
- Fast processing
- Good heat resistance
- Processed with cold mold (24°C)
- Compostable

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Ingeo AW 300D
Injection molding typical properties

Typical Material & Application Properties		
Physical Properties	**AW 300D**	**ASTM Method**
Specific Gravity	1.34	D792
MFR, g/10 min (210°C, 2.16kg)	27	D1238
Peak Melt Temperature (°C)	170	D3418
Mold Shrink in/in	0.003 – 0.006	D955
Clarity	Opaque	
Mechanical Properties		
Flexural Modulus, kpsi (MPa)	355.3 (2450)	D790
Notched Izod Impact, ft-lb/in (J/m)	0.62 (33)	D256
Vicat Softening Point, °F (°C)	225 (107)	D1525
HDT at 66 psi (0.455 MPa), °F (ºC)	122 (50)	D648

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Ingeo AW 300D

Processing recommendation starting points, may need to be optimized

Processing Temperature Profile		
Melt Temp.	375-410ºF	190-210ºC
Feed Throat	70ºF	20ºC
Feed Temp.	350-365ºF	175-185ºC
Compression Section	355-385ºF	180-195ºC
Metering Section	375-410ºF	190-210ºC
Nozzle	375-410ºF	190-210ºC
Mold	75ºF	25ºC
Screw Speed	100-200 rpm	
Back Pressure	50-100 psi	

Injection and Cooling Parameters	
Injection pressure, psi (MPa)	5500 (38)
Injection time, s	2
Hold pressure, psi (MPa)	6500-9500 (45-65)
Hold time, s	5-50
Cooling time, s	4

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Ingeo AW 300D key benefits for injection molded food serviceware

- Polypropylene type feel
- Good impact strength / ductility
- Fast processing
- Good transfer of mold detail
- Moderate heat resistance
- Processed with cold mold (30°C)
- Compostable

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Food service articles produced from Ingeo AW 240D and Ingeo AW 300D

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Ingeo AW 300D and Ingeo AW 240D

- Currently under evaluation for compliance with compostability standards

- USA: as a component in “housewares”–such as disposable food service articles grades are in compliance with FDA regulations

- EU: All monomers and additives are listed in Regulation 10/2011

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Ingeo PLA Grade Extension

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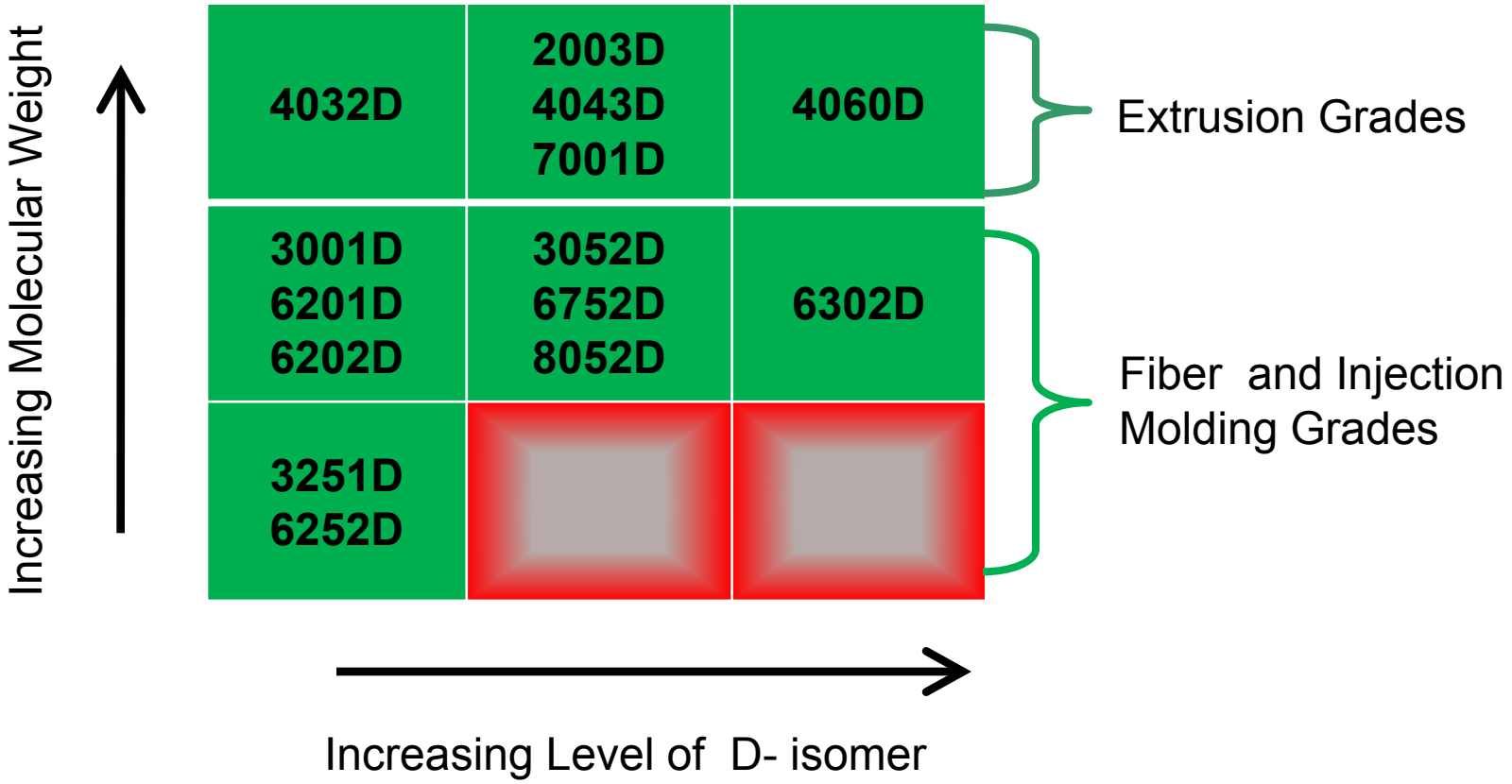
Previous design table – Ingeo™ PLA grades



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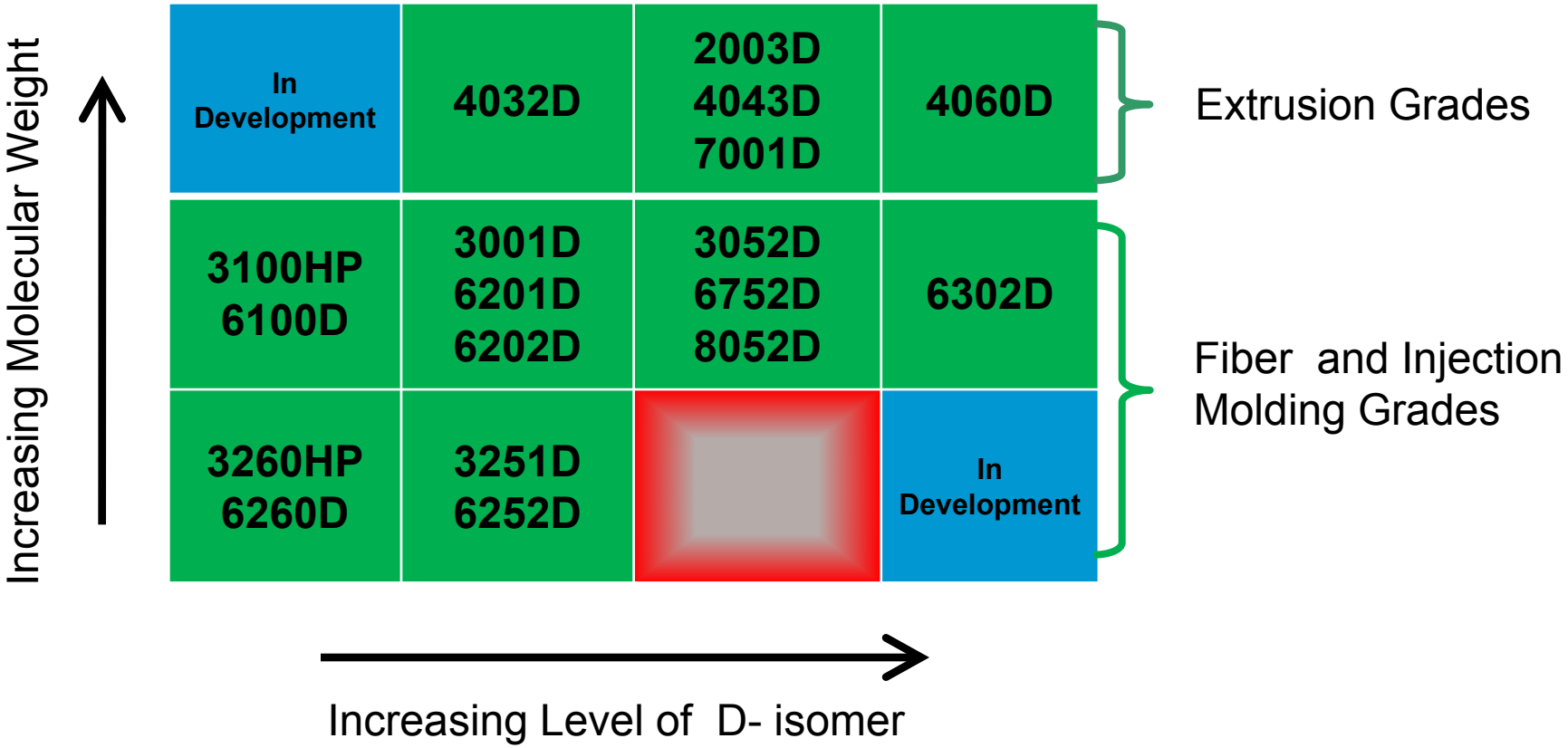
Expanded design table – Ingeo™ PLA grades



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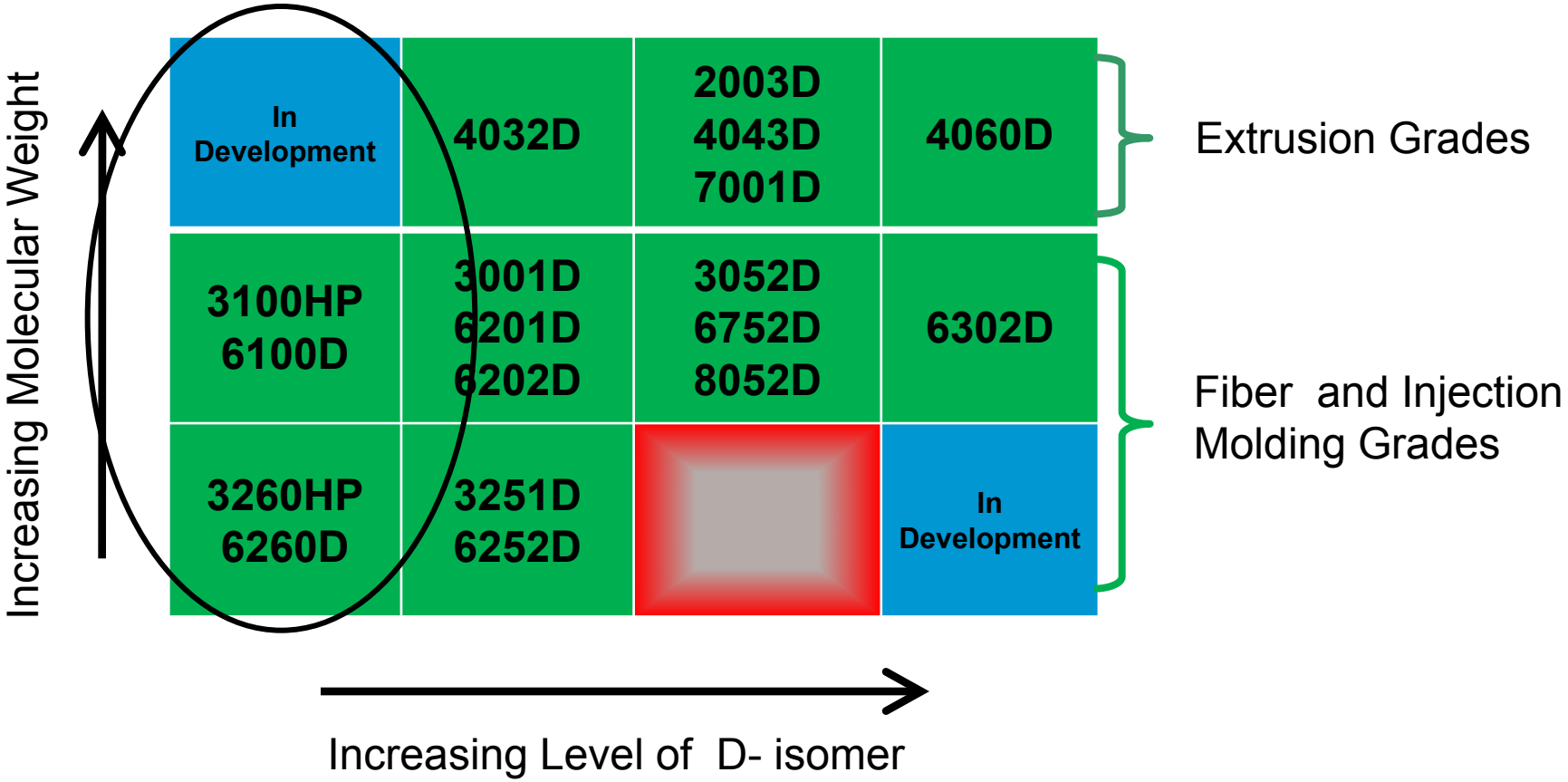
Expanded design table – Ingeo™ PLA grades



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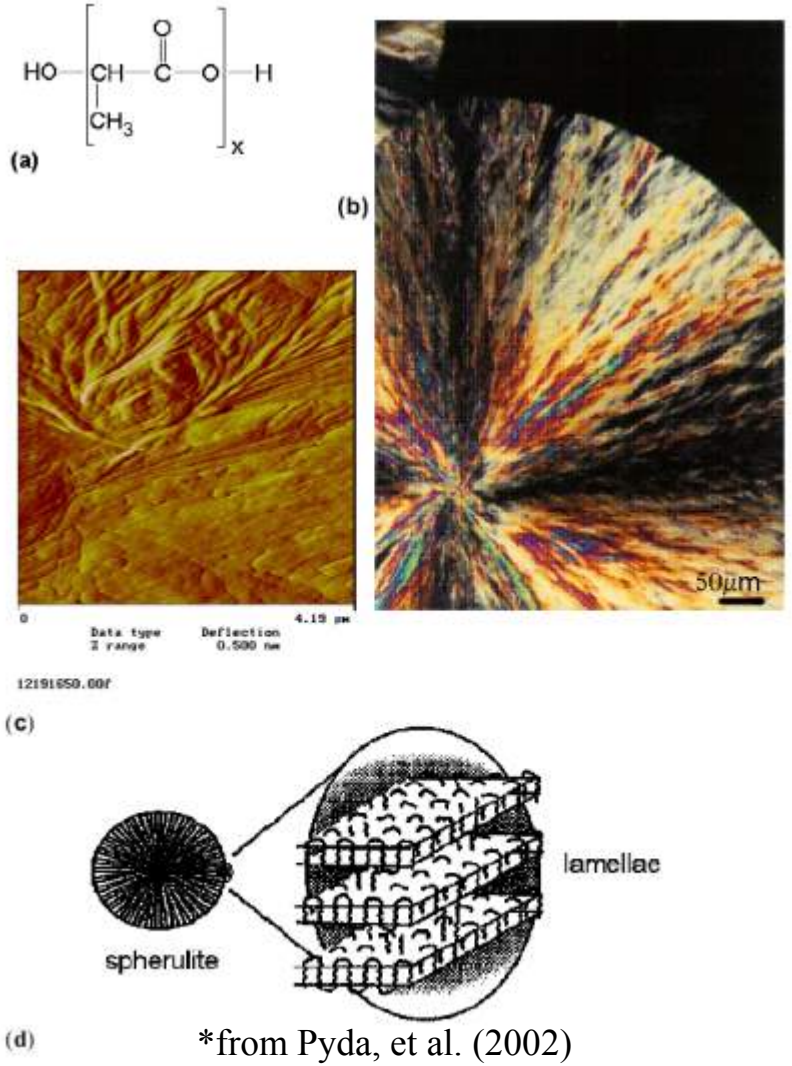
Properties of New Ingeo Grades with High Productivity and High Performance

New High %L Family

Quiescent crystallization



*from Pyda, et al. (2002)

- Generally spherulitic
- Follows Avrami kinetics

$$k = \frac{4}{3}\pi N G^3 \quad x = 1 - e^{-kt^n}$$

Where x = fraction of crystallinity and n=3

- Dominated by slow crystal growth, G
- Enhanced by nucleation, N
- Size of spherulites after impingement is dominated by N
- Applied when crystallizing pellets or annealing processes
- Highly sensitive to optical comp. and T
- ΔH of pure crystal = -93.1 J/g

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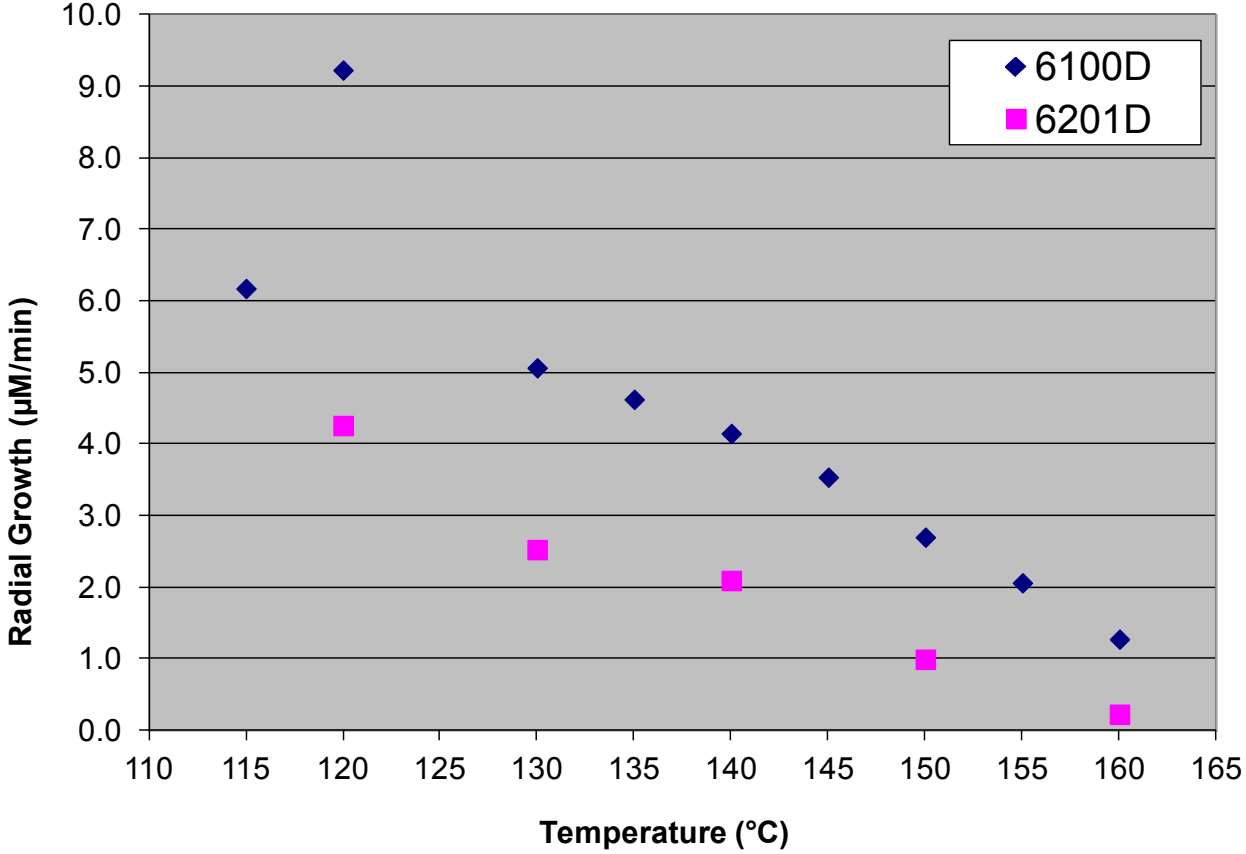
High %L crystal growth rate results

Hot stage microscopy measuring lineal crystal growth rate

	#	%D	RV
R	6100D	0.3	3.1
	6201D	1.5	3.1



Crystal radial growth shows > 2x increase as f(T) over today's product offering

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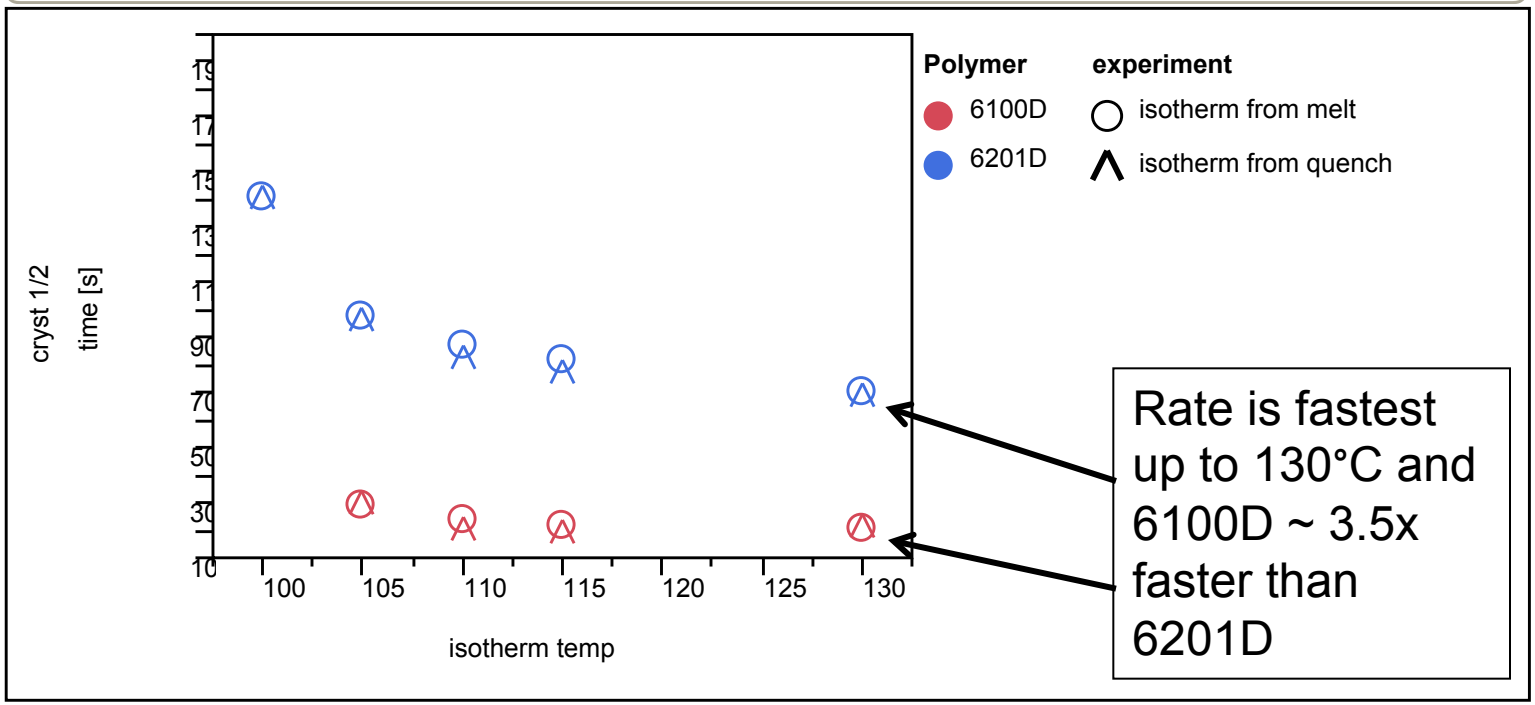
1.0% LAK-301 nucleant crystallized from the melt and quenched states

Bivariate Fit of cryst 1/2 time [s] By isotherm temp Nucleant=1% LAK-301



LAK-301 supplied by Takemoto Oil & Fat

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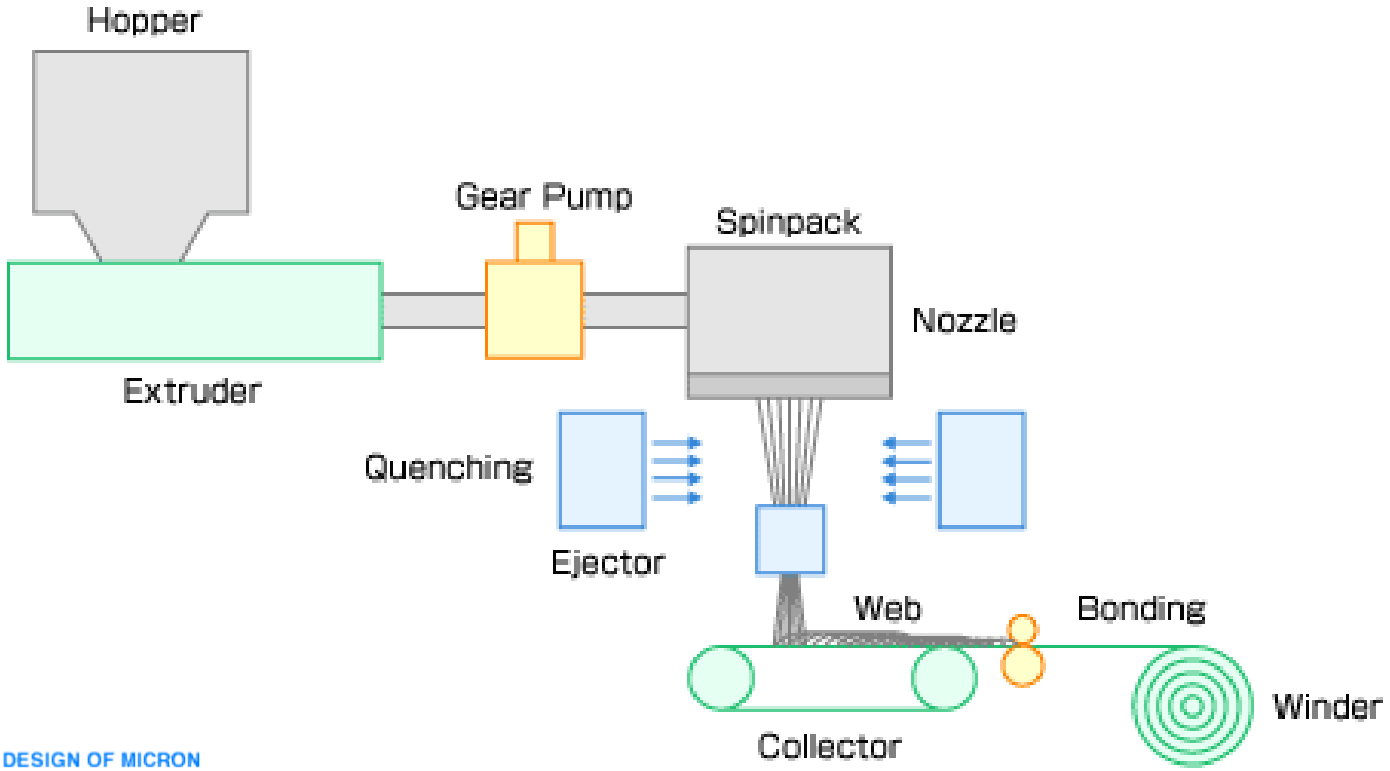
Spunbond Process



DESIGN OF MICRON
Kasen Nozzle Mfg. Co.,Ltd

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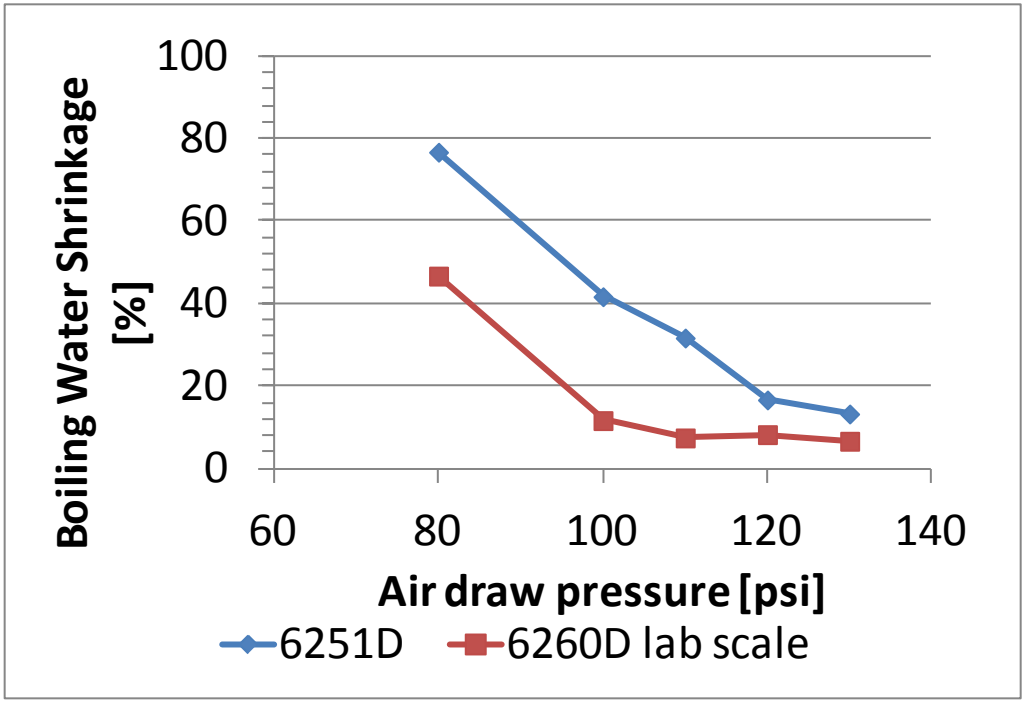
Spun bond fiber shrinkage

Lurgi Gun spun bond simulation
144 holes at 0.3mm diameter
0.75 g/min/hole
Draw down range = 18-21
Filament velocity range = 2800-3800 m/min
220°C melt temperature, 800-900 psi



6260D processes with lower shrinkage at lower air draw pressures compared to 6251D standard material

Increasing velocity and cost

Increasing asset age

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Advantages of expanded offering in fibers

- Broad range of applications, with lower shrinkage expected across the board
  - Nonwovens (3-4% shrink melt blown)
  - Drawn and heat set fibers
- Higher modulus above T_g
- More hydrolysis resistant
- Heat setting at higher temperatures leads to higher melting / sticking points during processing and use
- Higher T_m has advantages in bicomponent systems, broadending process windows

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Bulk crystallization: nucleation study

- Crompton, Kemamide EBS at 0.5 wt%
  - ethylene-bis-stearamide
  - 140°C T_m, flash point 280°C
- Nissan Chemical, Ecopromote at 1.0 wt%
  - phenylphosphonic acid, zinc salt
  - decomposition >500°C
- Takemoto Oil & Fat, LAK-301 at 1.0 wt%
  - aromatic sulfonate derivative
- Specialty Minerals, Ultratalc 609 at 0.5 wt%
  - 0.9 µm mean particle size Montana talc, untreated

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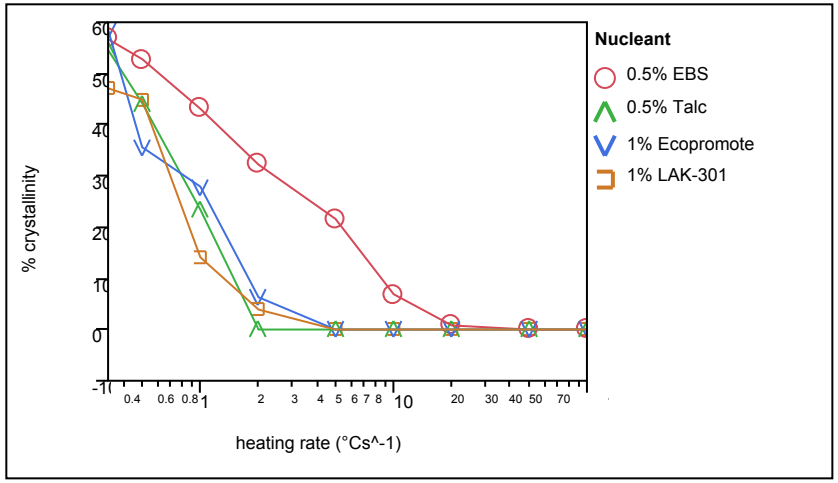
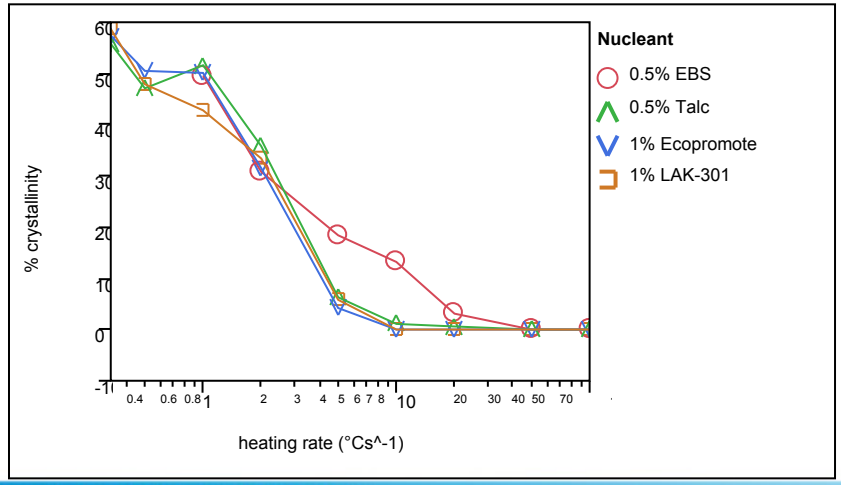
Crystallization during varied heating rates

Ingeo 3001D (~1.5%D) vs. 3100HP (~0.3%D) at equal MW with Four Nucleants

Analysis of % Crystallinity During Heating



3001D + nucleants heating at
0.5-100°C/sec second
From the quenched state (30°C)



3100HP + nucleants heating at
0.5-100°C/sec second
From the quenched state (30°C)

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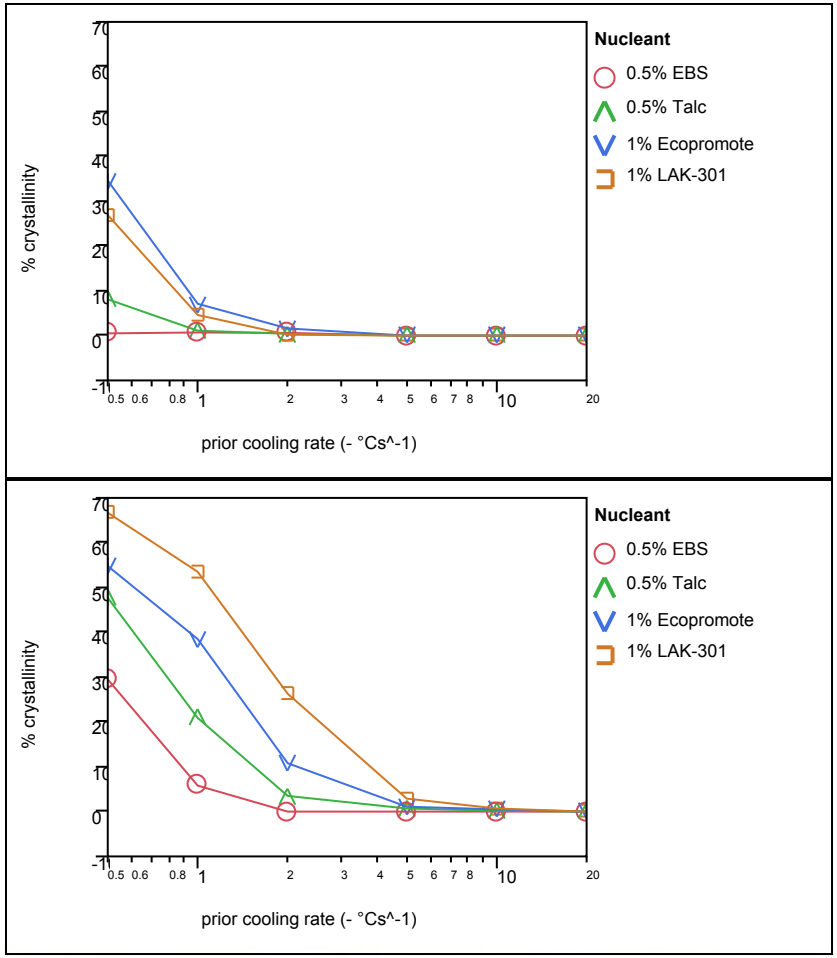
Crystallization during varied cooling rates

Ingeo 3001D (~1.5%D) vs. 3100HP (~0.3%D) at equal MW with Four Nucleants

Analysis of % Crystallinity During Reheat at 100°C/sec



3001D + nucleants cooling at
0.5-20°C/sec second
From the molten state (210°C)

3100HP + nucleants cooling at
0.5-20°C/sec second
From the molten state (210°C)

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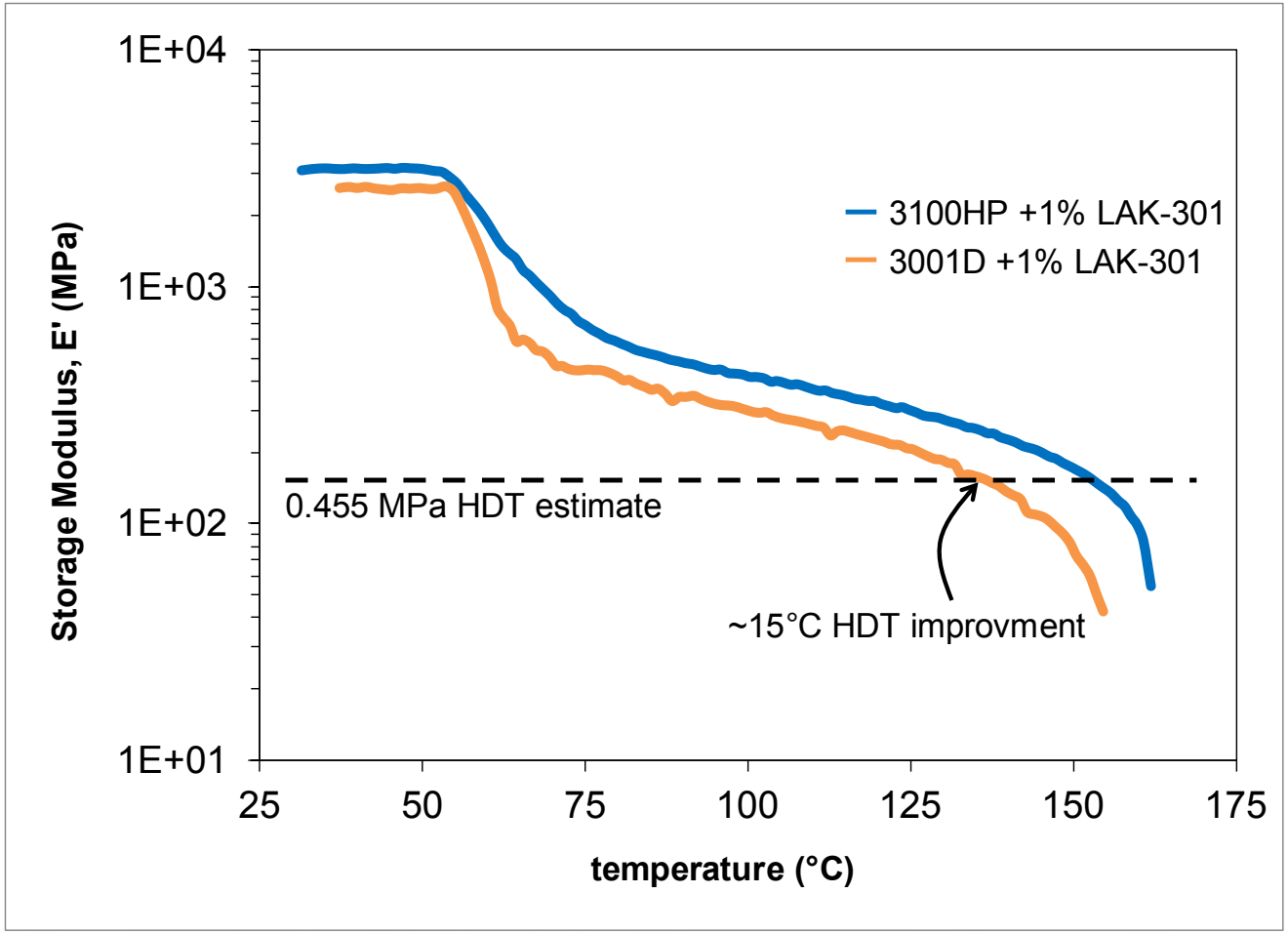
Stiffness of hot molded bars with nucleant, 3 point bend geometry to measure E'



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Advantages of expanded offering for the durable & semi-durable market

- Compounders can produce more competitive materials
  - Higher productivity during molding
  - Wider processing window
  - Simpler & more cost effective formulations
  - Improves base performance the Ingeo 3801X
- Potential for higher bio-content in formulations
- Higher modulus above T_g, higher HDT
- Higher hydrolysis resistance
- Improved performance in extruded & thermoformed durable applications

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Timeline for commercialization

- Ingeo 6100D, 3100HP, 6262D and 3262HP are scheduled to be available 2Q2013

- Expect further publications and process guides from NatureWorks throughout the year

*Note all data shown for Ingeo 3100D, 6100D, 3260D and 6260D in this presentation were from product development samples, and some changes are expected with large scale commerciallization. No descriptions or results shown are specifications for these materials.

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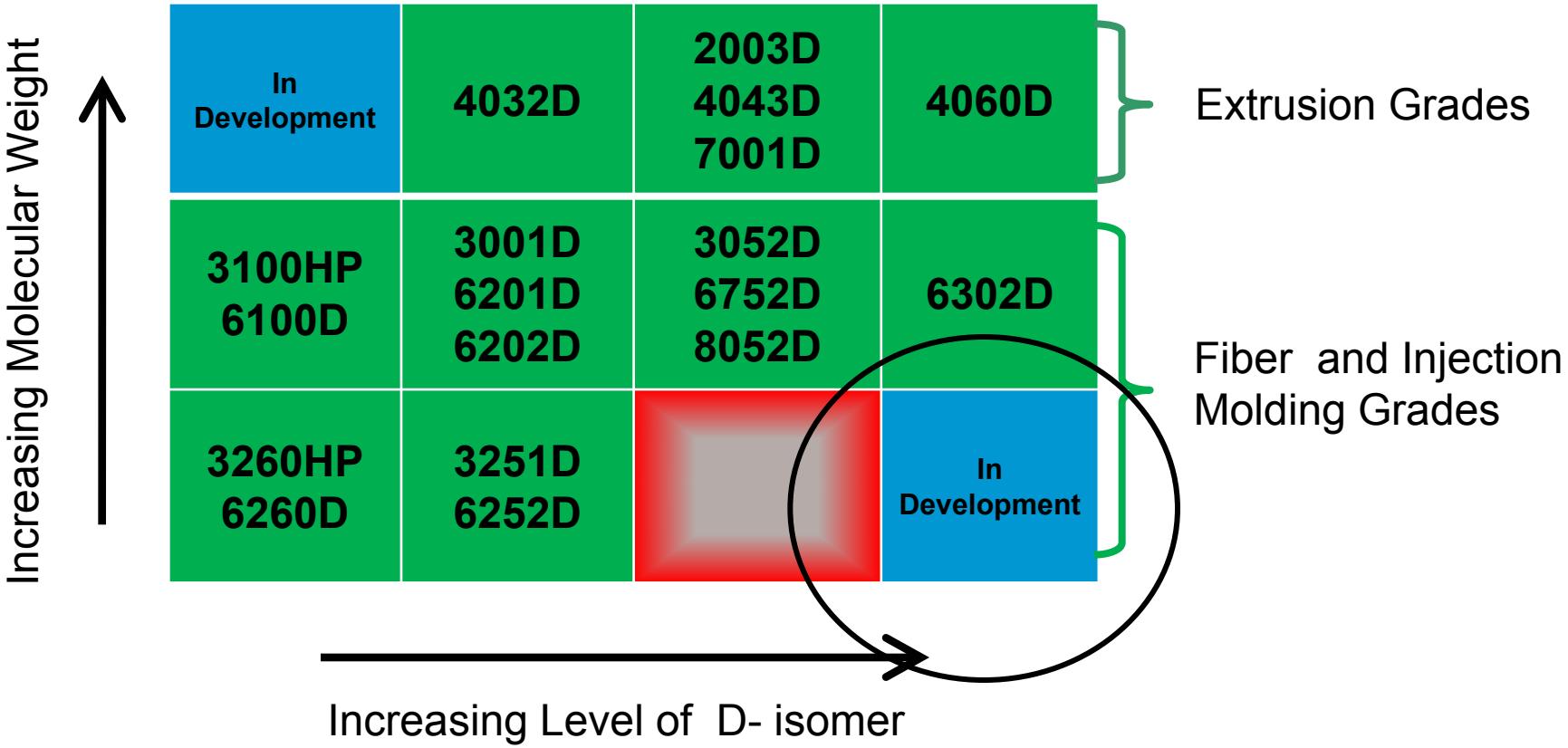
Expanded design table – Ingeo™ PLA grades



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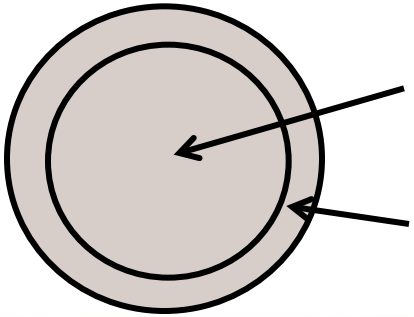
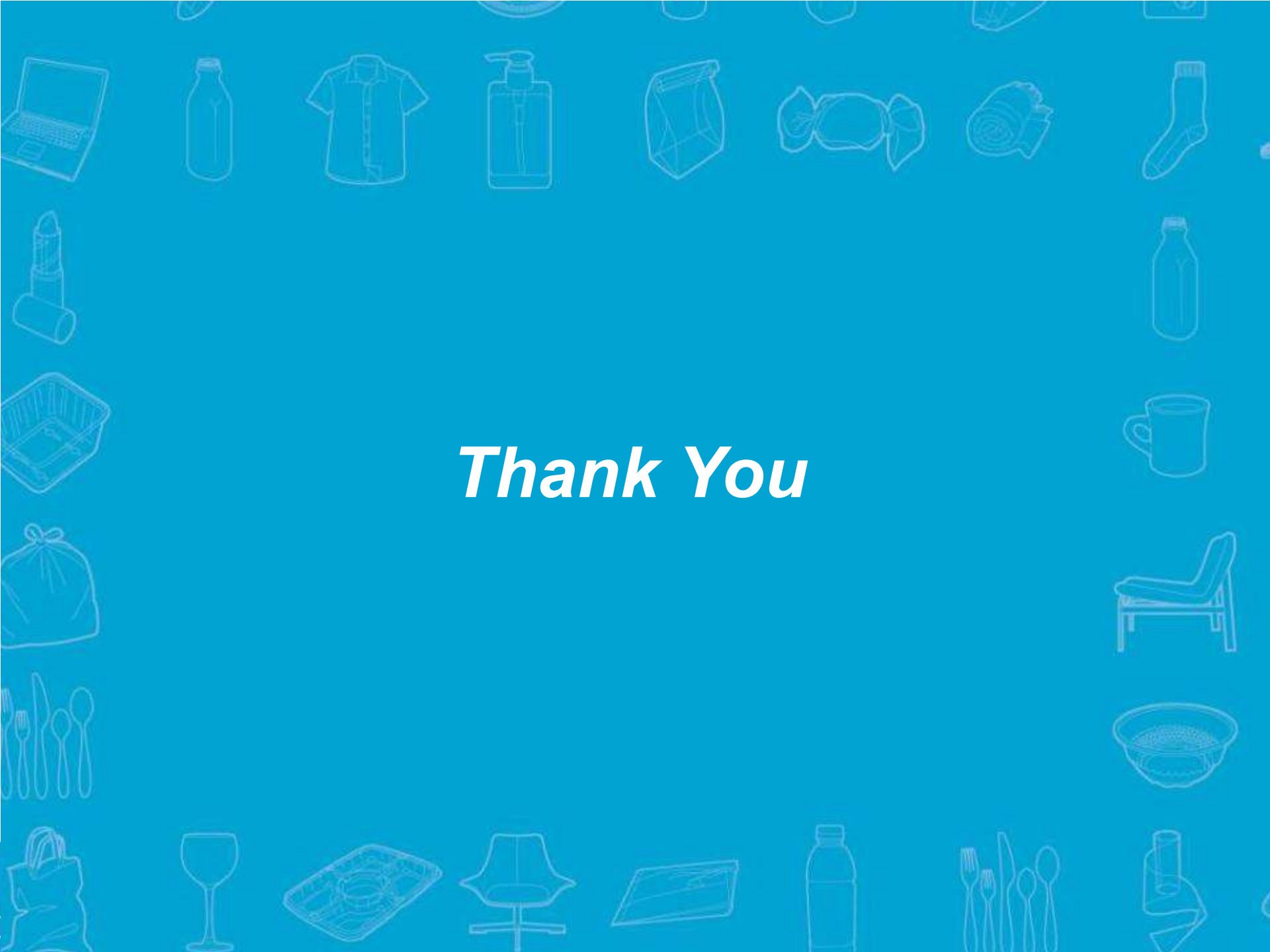
High flowing Ingeo PLA binder now in development

- High flow characteristics
  - ~40 g/10 min MFI at 190°C
- Low viscosity, high % D amorphous
- Useful for binder / heat seal in multicomponent fiber structure
- Useful to seal on to itself, other polymers or other materials such as cellulose
- Available for sampling




Thank You