Properties, Strengths and Weaknesses of PLA and other Biomaterials.

ME BIOPLASTICS

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Jim Lunt & Associates LLC

The Evolving Biobased Plastics Landscape

Feedstocks

Agricultural building blocks

Polysaccharides
- Starch/Sugars
- **Lignocellulosics**
  - -wood
  - -straws, stover etc.
- **Others**
  - - Pectins
  - - Chitosan
  - - Gums

Fats/proteins
- **Animals**
  - - Oils
  - - Casein
  - - Whey
  - - Gelatin
- **Vegetable**
  - -oils
  - - Zein
  - - **soybean protein**
  - - Gluten

Polymers

Direct Fermentation

Polyhydroxy alkanoates PHA's
- PHB
- **PHBV**

Bio-technological Origin

PLA
Nylon 11
Polyethylene
Polypropylene
Polyisoprene
Aliphatic Polycarbonate

Petroleum/ Natural based

Starch blends
Nylon 6,10
Nylon 6,12
PTT
PBS
Polyurethanes

Global Biobased Polymer Capacities for Major Players

Product	Company	Location	Capacity/mt	Price/#
PLA	Natureworks	USA	70,000	0.80-1.10
PLA	Hisun	China	5,000	1.25
PHA's	Metabolix	USA	300/50,000 - 2009	2.50
PHAH	Meredian	USA	150,000?	n/a
PHBV	Tianan	China	2,000	2.40-2.50
Materbi	Novamont	Eu	75,000	2-3
Cereplast	Cereplast	USA	25,000	1.50-2.50
HDPE	Brazchem	SA	200,000 -2009	0.80-1.00

Comparative Material Properties of PLA

	s.g.	Tg, C	Tensile Strength Mpa	Elongation, %	Flexural Strength Mpa	Flexural Modulus Mpa	Izod Impact, J/m
aPLA	1.24	58	53	6	83	3800	12.8
PS	1.05	85	45	47	76	3000	21
aPET	1.39	69	57	70	88	2700	59

Comparative
Gas Transmission Properties of PLA

Resin	OTR	WVTR	CO_2
PLA	**38-42**	**18-22**	**201**
PET (OPET)	3-6.1	1-2.8	15-25
HDPE	130-185	0.3-0.4	400-700
PP	150-800	0.5-0.7	150-650
Nylon 6	2-2.6	16-22	10-12
EVOH	0.01-0.16	1.4-6.5	
PVC	4-30	0.9-5.1	4-50

Key Challenges of PLA Today

- Glass transition of 58^0C.
- Low melting point for fibers – cannot be ironed .
  - ✓Poor abrasion resistance
  - ✓ Low temperature dyeability –poor color fastness
- Low heat resistance in clear thermoformed and injection molded articles due to poor crystallization speed.
- High moisture vapor, oxygen and carbon dioxide transmission.
- Low impact resistance.
- High Density compared with PS, PP, PE but lower than PET.
- Not designed for durability.

Key Product Improvement Programs

- Improved heat resistance without sacrificing clarity
  - PLA's heat resistance in clear, amorphous thermoformed packaging typically governed by Tg, which is 58^{o}C.
  - PLA's Crystalline melt temperature is 150-170^{o}C.
  - Increased heat resistance, decreases the need to manage the supply chain in hot climates.

- Improved impact resistance without sacrificing clarity
  - Non orientated PLA products are more brittle compared with Impact modified PS, PET or PVC packaging

- Improved barrier to water vapor, oxygen and carbon dioxide

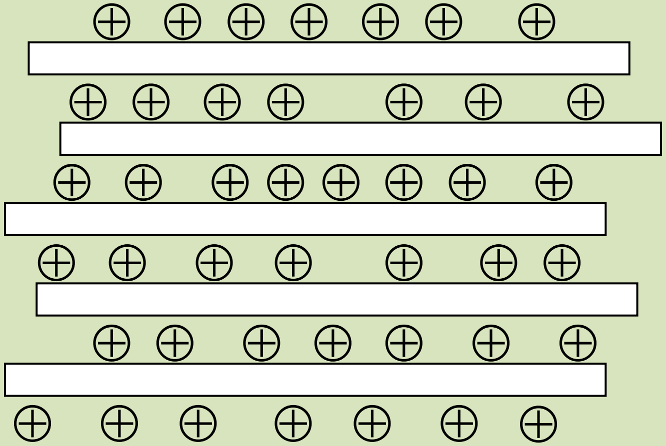
Improved Heat Resistance Options for thermoforming

- Copolymers-some options but longer term program.
- Cross linking –No Practical routes found to date.
- Fillers – relatively ineffective in amorphous systems and generally opaque.
- Higher heat PLA (stereo complex)- feasibility demonstrated on lab scale .
- Polymer blends –demonstrated.
- Nucleation to provide relatively clear crystalline parts – demonstrated commercially.

PLA Nanocomposite Program

Key Properties of Montmorillinite

- *Shape: Platelet*
- *Size: 1nm thick, 75-150 nm across*
- *Charge: unit cell 0.5-0.75 charge*
  92 meq/100g clay
- *Surface Area: >750 m^2/g*
- *High Modulus: ~170 GPa*
- *Not abrasive*



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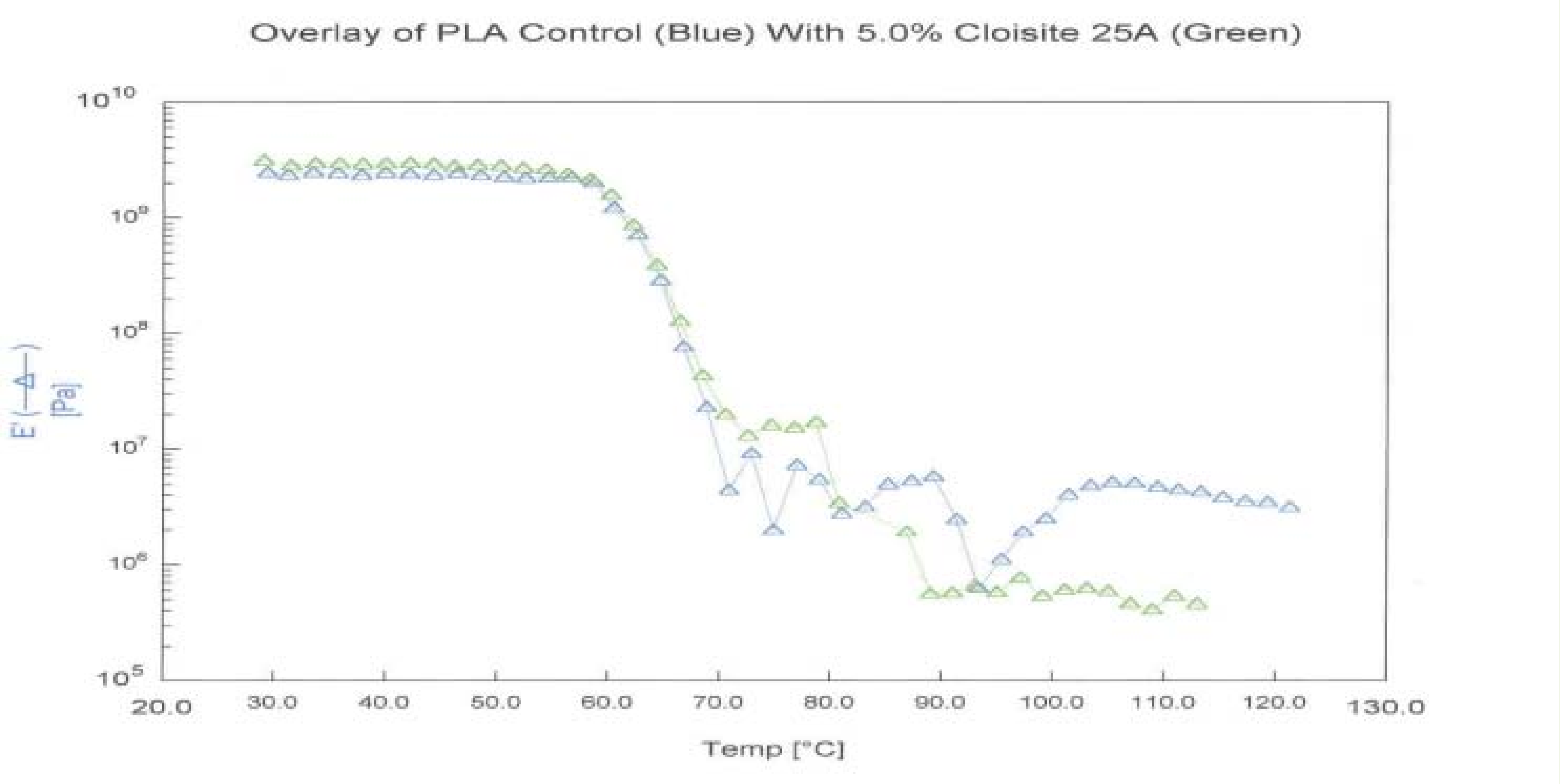
PLA Nanocomposite Program



<u>No Increase in Glass Transition Temperature.</u> *(In agreement w/ S. Sinha Ray et al., for both Intercalated and Exfoliated PLA Nanocomposites, Nanocomposites 2002.*

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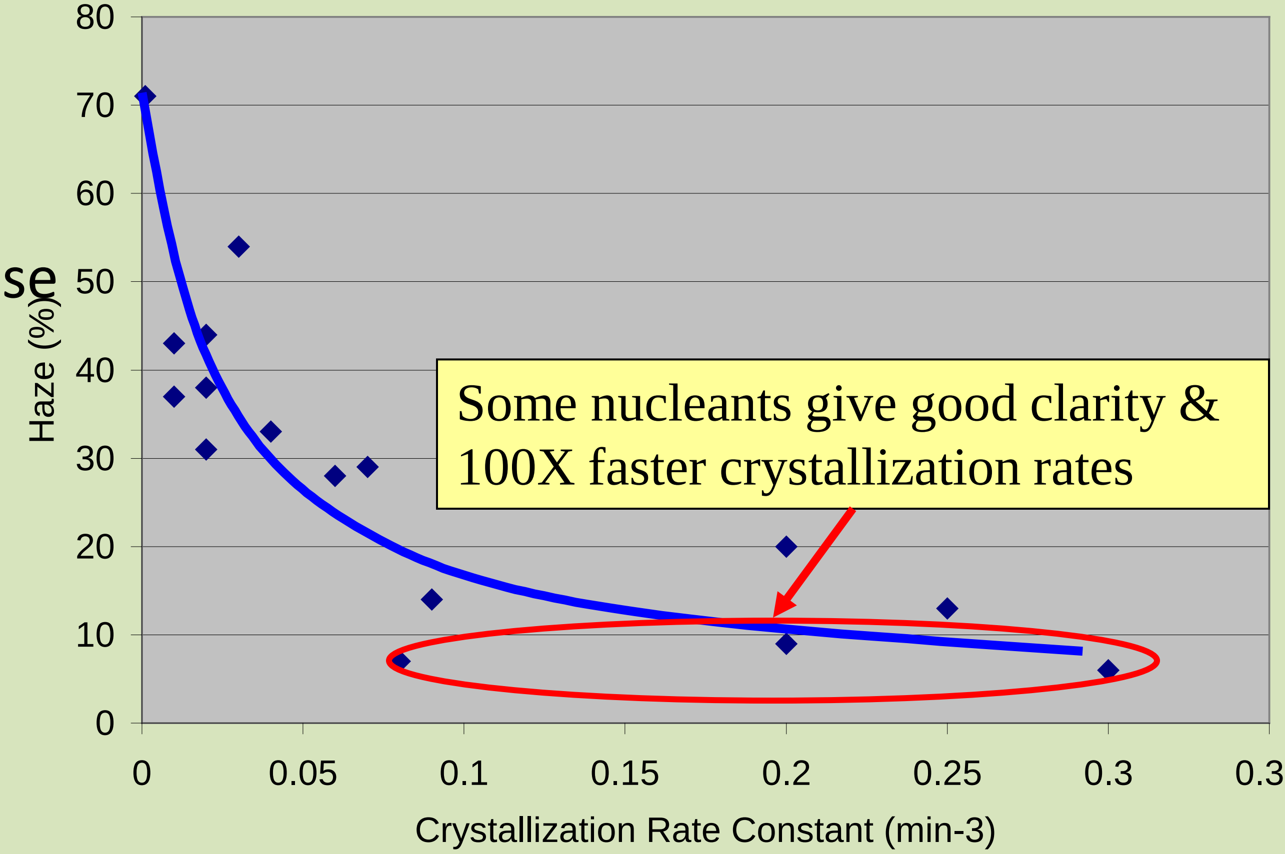
Nucleating Agents Increase Crystallization Rates without Sacrificing Clarity

- Over 300 nucleating agents screened.
- Haze tends to decrease as crystallization rate increases for various nucleating agents.



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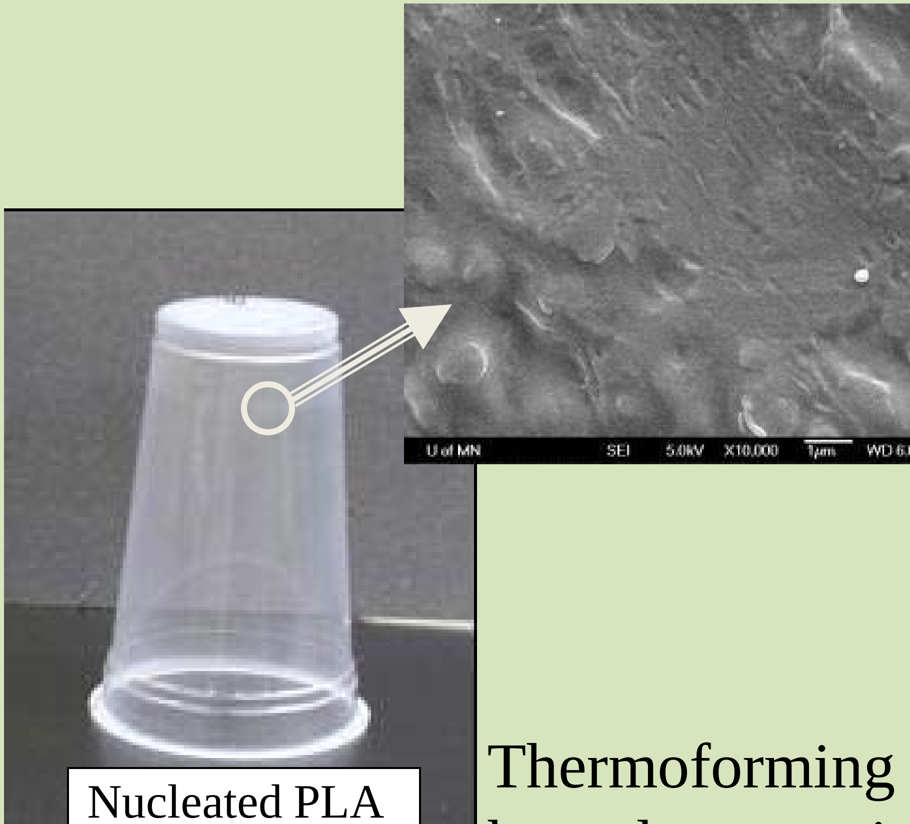
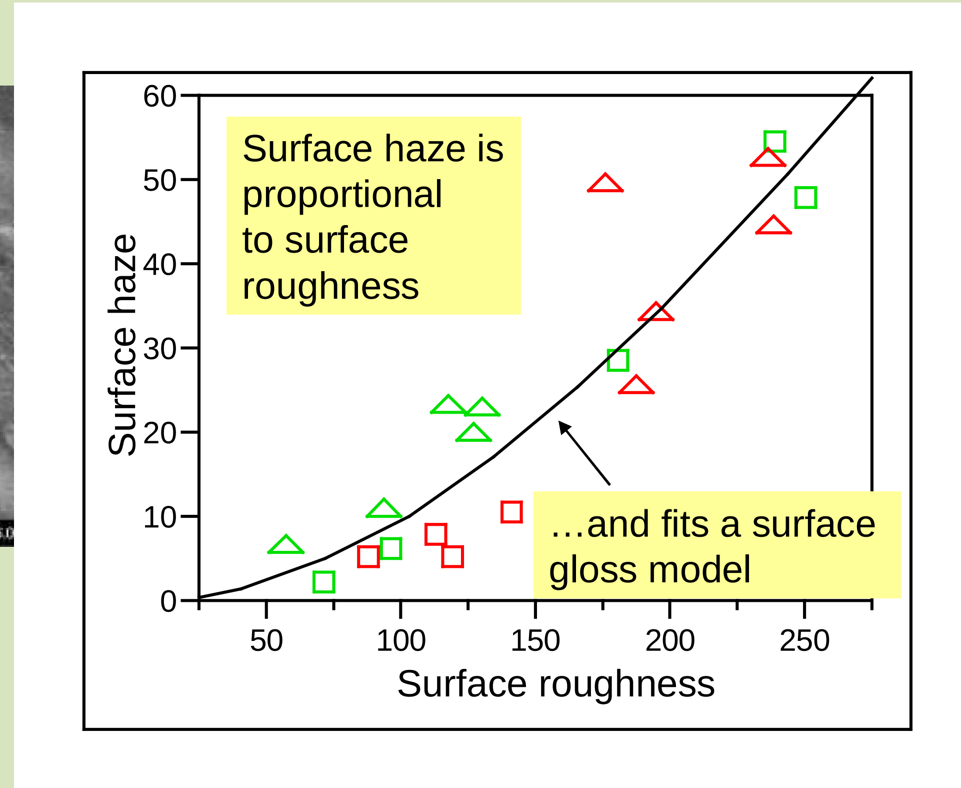
Thermoforming Nucleated PLA Can Result in Higher Heat Resistance But With Higher Haze

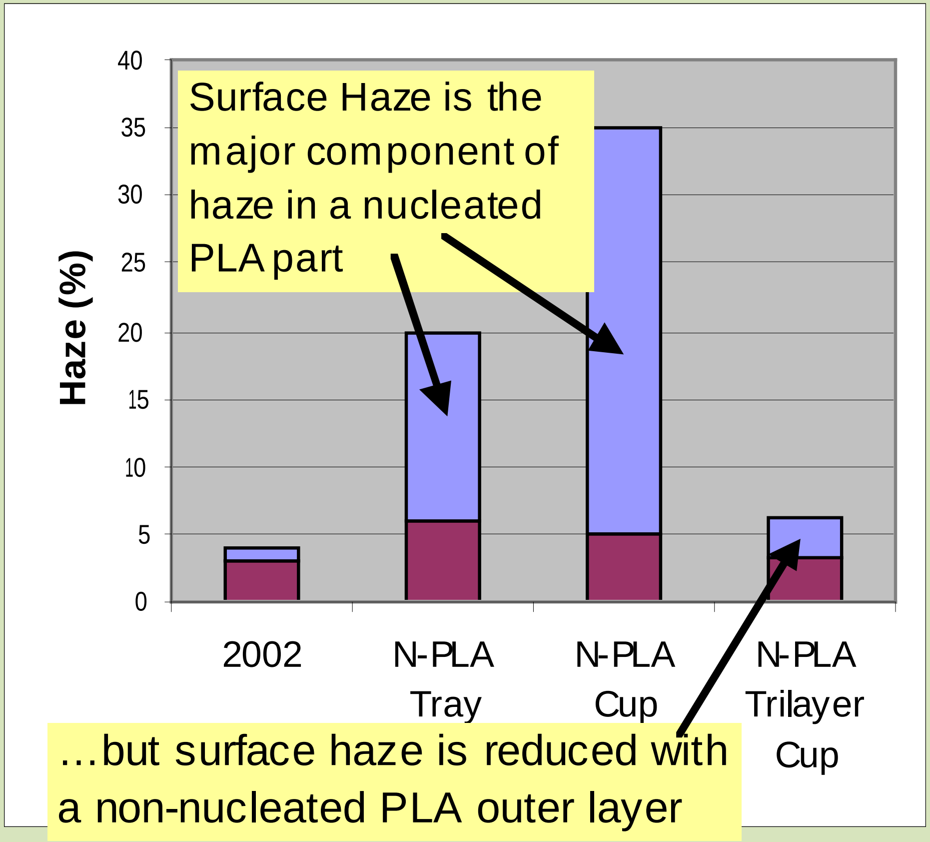




Thermoforming nucleated PLA parts tends to increase haze due to an increase in surface roughness

Restoring Clarity to Nucleated PLA Parts by Addressing Surface Roughness

- Surface roughness can be decreased & haze reduced
- Trilayer sheet is one option.
- Other options are being explored.



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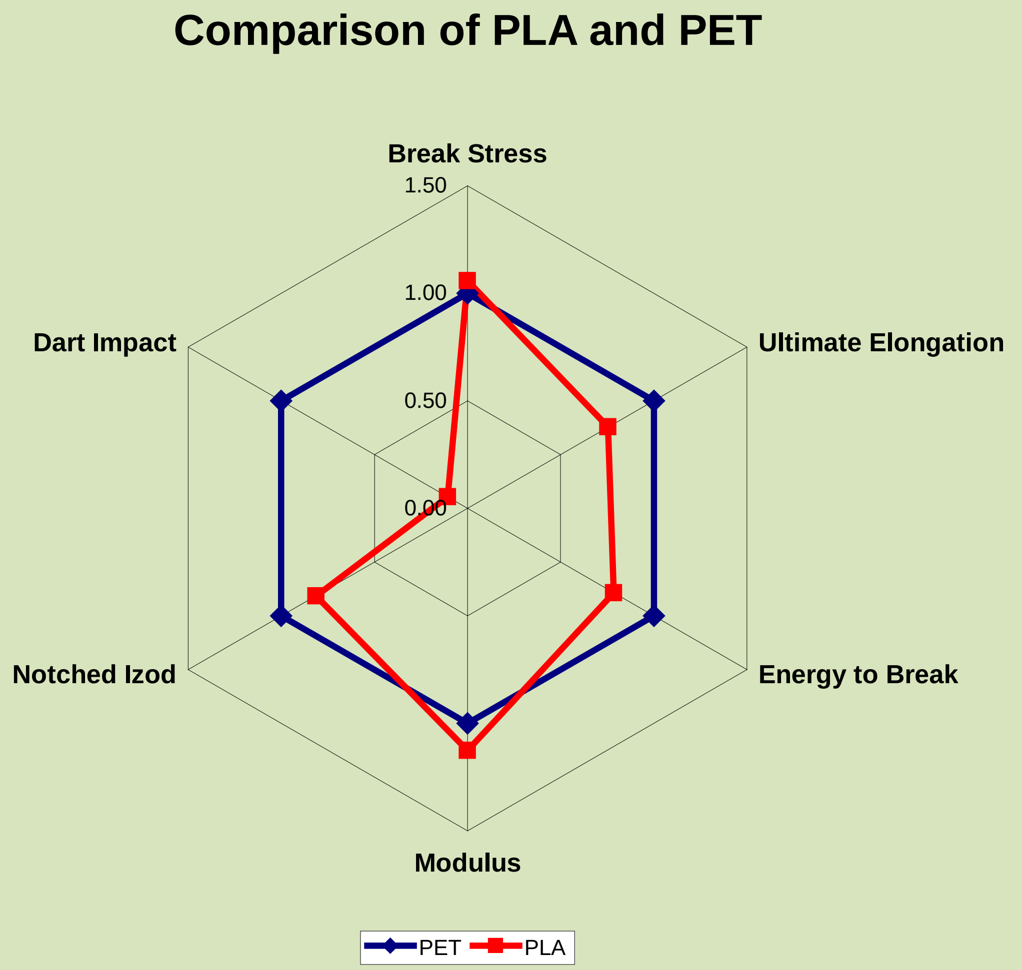
PLA Impact Performance

- PLA may be more brittle than desired is some applications.
- Goal is to improve impact performance relative to a PET benchmark.
- Largest improvement needed in Dart Impact



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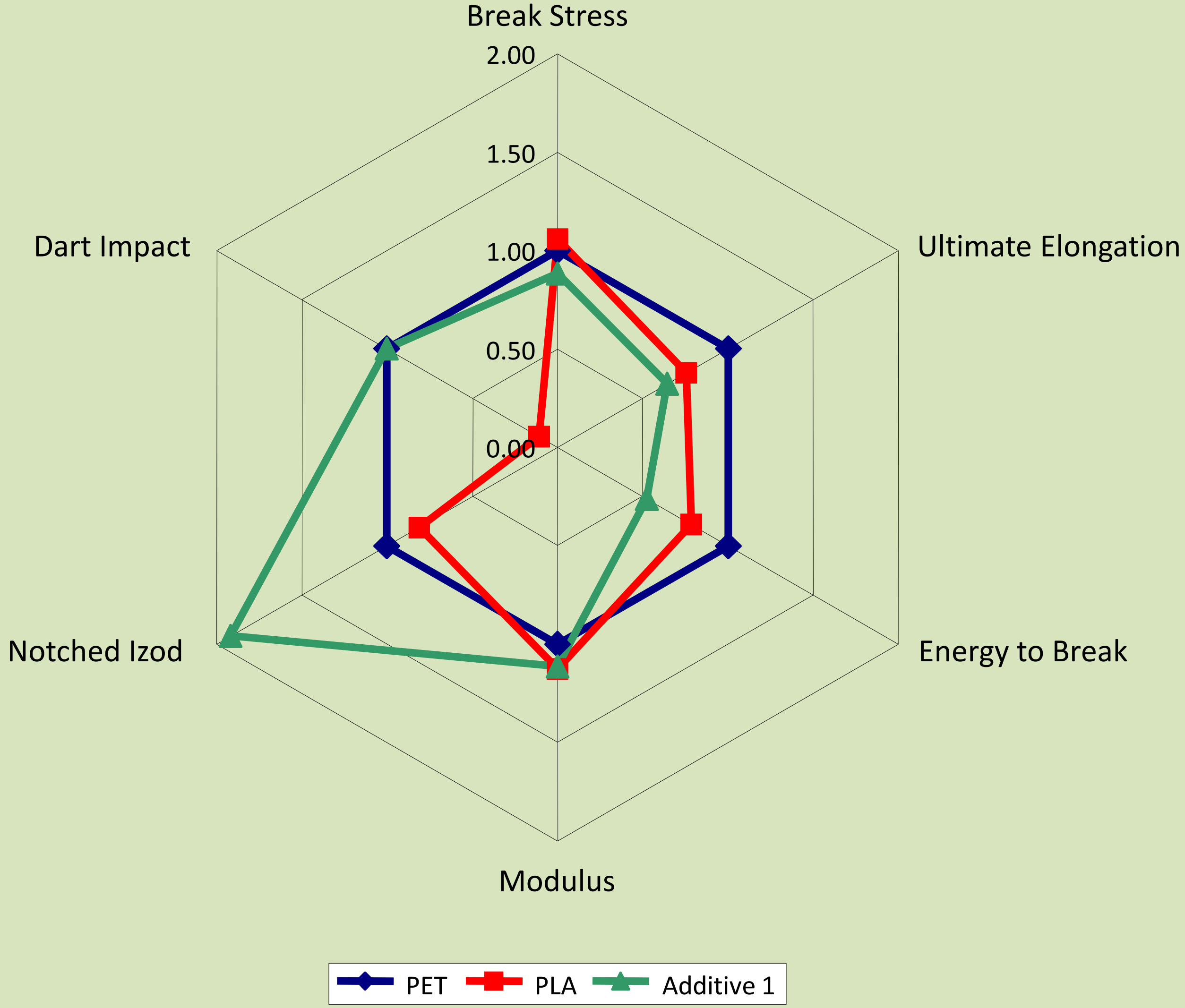
Improvement of PLA Impact Performance

Impact performance at or better than target can be achieved



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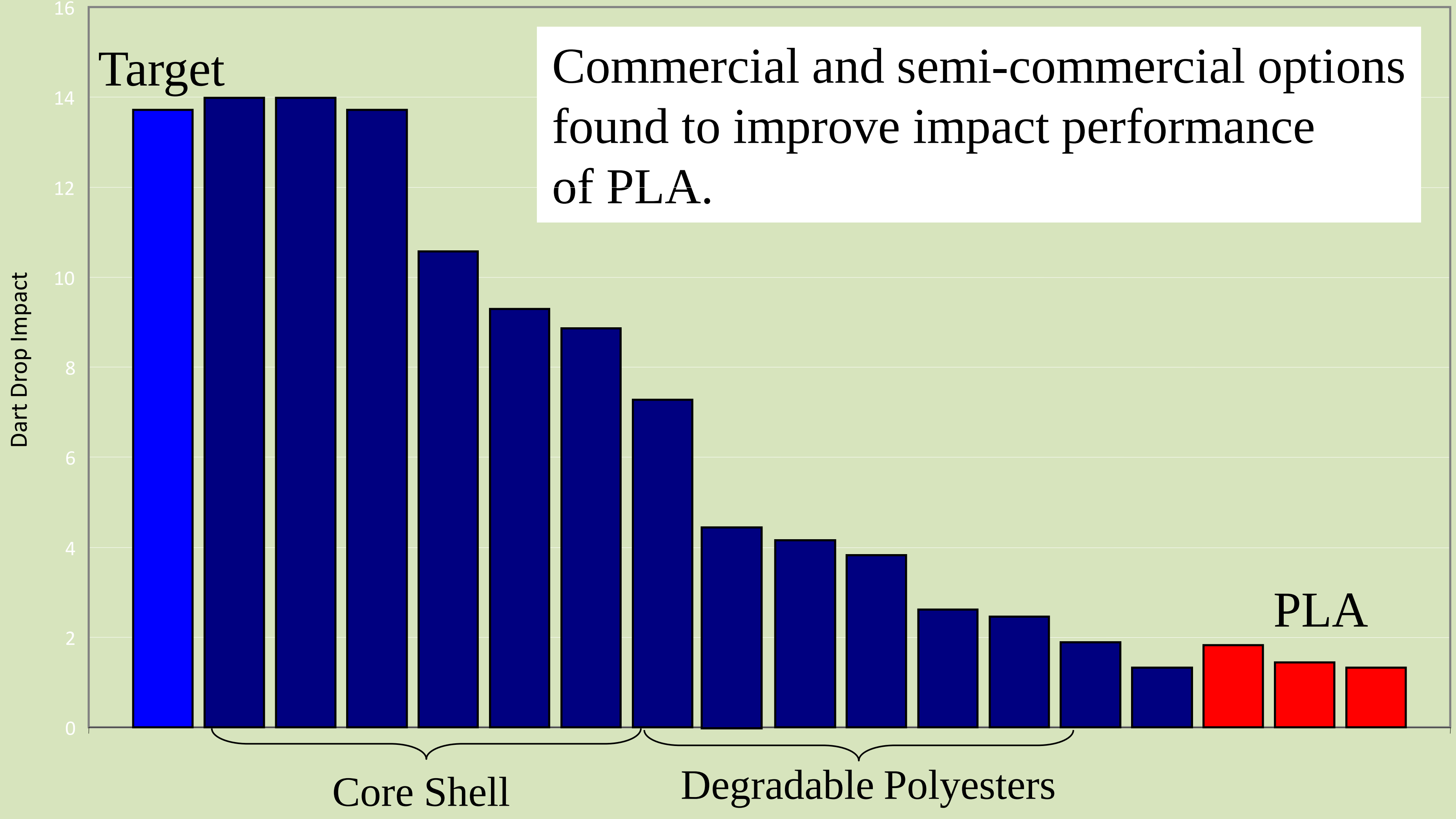
Range of PLA Impact Performance with Additives



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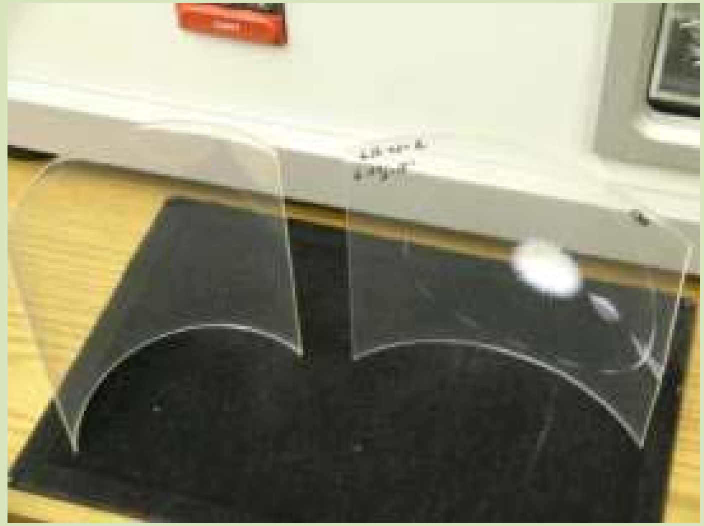
Commercial Impact Modifiers in PLA

			Tensile		
Additive	Loading	Dart Impact (ft.lb)	Energy to Break (in-lb)	Elongation (%)	Modulus (kpsi)
Blendex 338	5	13.7*	37.6	198	128
Clearstrength 320	5	10.6	17.4	97	119
Paraloid BTA 753	5	10.6	24	153	119
Ecoflex F	15	2.6	7.1	220	115
PLA	0	0.2	4.9	17	131

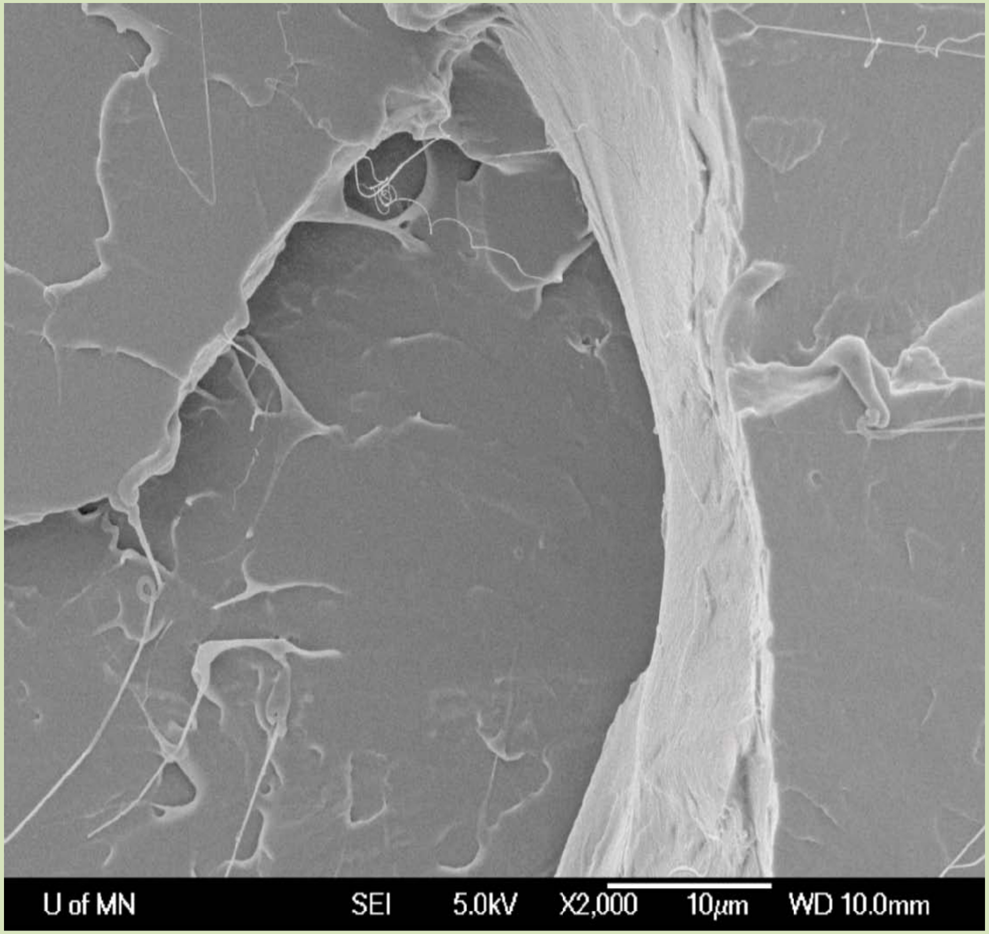
Dart Impact based on ASTM 1709-98 on 6x6" sheets 15 mil thickness
Tensile based on ASTM D882 on 4" dogbone samples cut from 15 mil thickness sheet, 2"/min elongation rate
*Test equipment maximum

Impact Resistance Improvement of PLA



Attributes	Blendex	Acrylic	Ecoflex	Biax PLA
Performance (Impact ft.lb)	>13.9	6 - 13.9	2 - 13.9	>13.9
Cost (material)	$0.05	$0.06 - 0.08	$0.20 - 0.23	Sheet
Clear (haze %)	opaque	6 - 9	opaque	9
Compliant (food)	no	Yes – Room Temp & Below	possible	FCN
Compostable	no	no	possible	yes
Commercially available	yes	yes	yes	converter

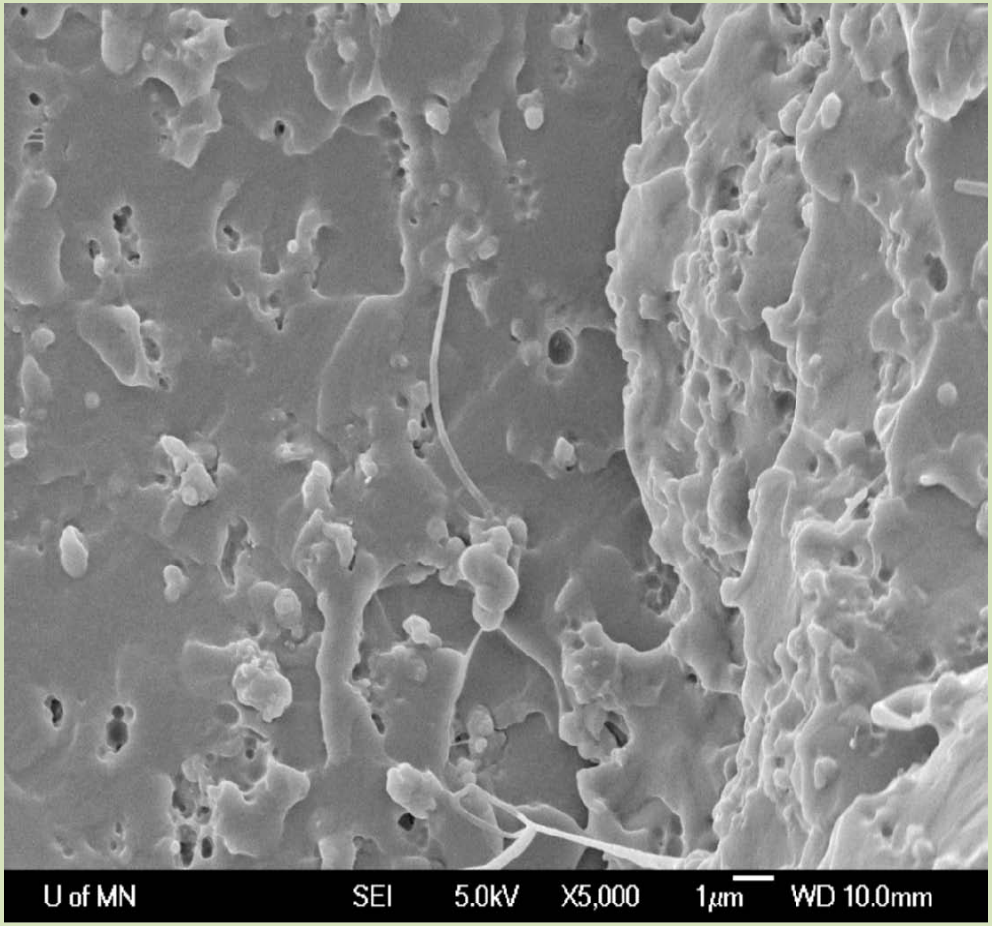
Base PLA Fracture Surface



Smooth fracture surfaces

Brittle failure mechanism

Impact Modified PLA – High Performance



- Good dispersion of modifier in PLA matrix
- Adhesive failure in the PLA, good adhesion between PLA and modifier
- Highly roughened fracture surface

Impact Improvement of PLA - Status

- Various additives excel in specific performance attributes
  - Improved impact performance
  - Good environmental profile
  - Required cost and availability
- No additive meets all target performance requirements
- Continuing search for modifiers that meet all targets
  - Commercial additives and blends

Impact Modified PLA: A PVC Replacement

Developed and commercialized in 2005

- PET Equivalent Impact Performance
- In the market today for gift cards
- Non-clear applications

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Property Deficiencies of other Bioplastics

Properties of PHB/PHBV

Specific Gravity	*1.25*
Yield Stress (MPa)	*37*
Tensile Strength (MPa)	*36*
Elongation at Break (%)	*5-10*
Tensile Modulus (MPa)	*1400*
Flexural Strength (MPa)	*61*
Flexural Modulus (MPa)	*1400*
Impact Strength (Kj /m^2)	*8*
Vicat Sofening Temperature (^{0}C)	*143*
Melt Processing Temp (^{0}C)	*180*
Melt Temperature (^{0}C)	*167*
Cystalisation Temp. (^{0}C)	*109*
Degree of Crystallinity (%)	*46*

Key Challenges of PHA Products

- Low thermal stability - 180C processing temperature.
- Narrow processing window.
- Not yet truly commercial.
- High price.
- Not yet food contact approved except for PHBV in EU.
- Processing/Processing properties still largely unknown.

Key Challenges of Starch Based Products

- Opaque.
- Moisture sensitive.
- Low temperature resistance.
- Generally blended with Petrochemical based materials to improve functionality.
- Generally not designed for durability.

Additives Being Supplied For PLA

Company	Additive	Role
Du Pont	Biomax Series	Impact, Heat Resistance
Rohm & Haas	Acrylics	Impact Resistance
Arkema	Castor Oil Based	Impact Resistance
Dainippon Inc.	PLA copolymers	Flexibility/impact
BASF	Ecoflex	Flexibility
BASF/Arkema	Epoxidised Acrylic	Melt Strength
Danimer/ Polyone	various	Antistats/ slip agents
Clariant	Blowing agent	Foaming/ melt strength

(See recent article in Plastics Technology for more information on Additives)

Blending of Bioplastics

PHBV/PLA Blends

Courtesy of Peter Holland BV

Why Blends of PHBV/PLA ?

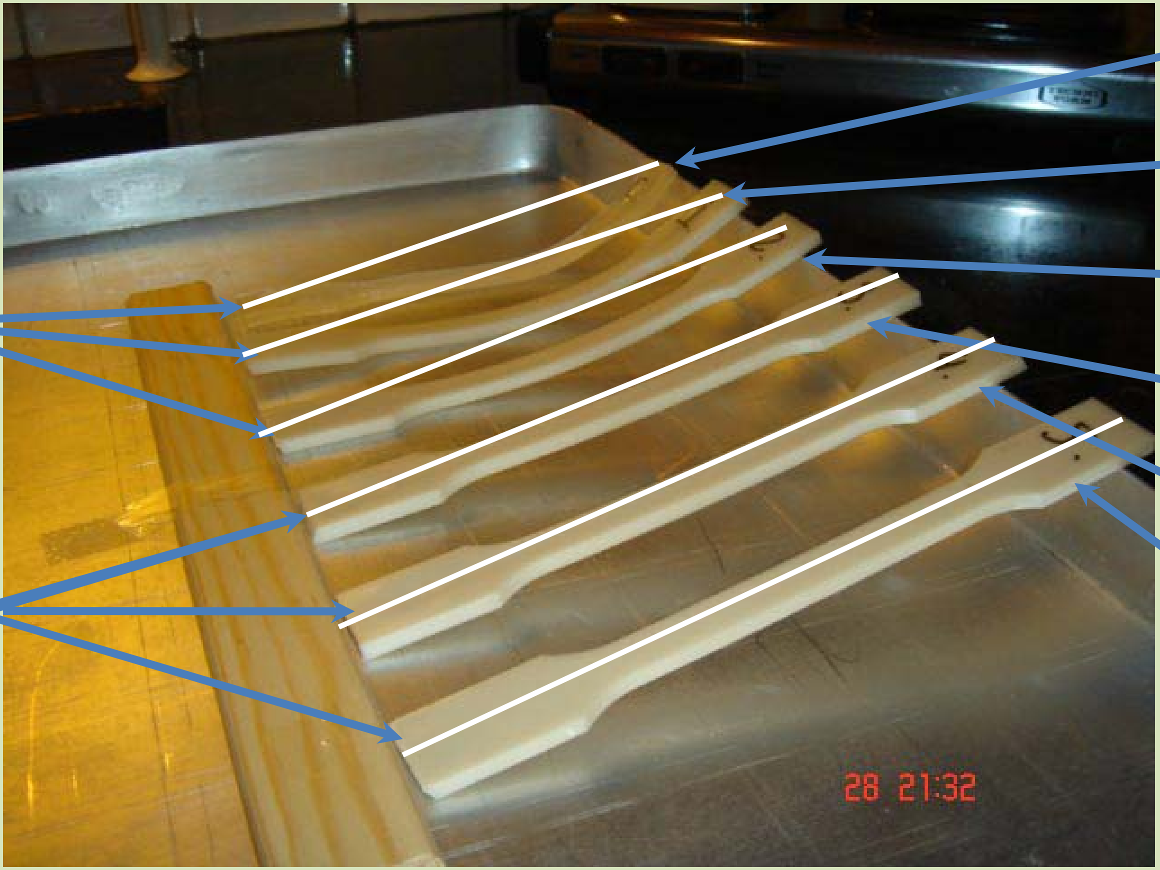
- Improved Temperature Performance over PLA
- Improved processing window over PHBV
- Wider mechanical property spectrum
- More versatility in formulation
- Almost completely renewable resource based

Heat Distortion Properties of PHBV/PLA Blends

Time

2Minutes Deformed

12Minutes Not Deformed



100%PLA

90%PLA/10%PHBV

80%PLA/20%PHBV

70%PLA/30%PHBV

60%PLA/40%PHBV

50%PLA/50%PHBV

Samples Held up to 12minutes at 100 C

COURTESY OF PETER HOLLAND BV

Heat Distortion Temperatures of PHBV/PLA Blends

Sample	Load MPa	HDT ^{o}C
100% PLA	0.45	52.0
90/10	0.45	53.4
80/20	0.45	54.5
70/30	0.45	54.6
60/40	0.45	63.0
50/50	0.45	66.3

PHBV/PBS/Ecoflex Blends

Why Blend With PBS?

- Improved flexibility over PHBV
- Potential alternative to replace Ecoflex in blends with PHBV
- Potential to be higher biobased content than Ecoflex blends
- More than one supplier of PBS

Typical Properties of PHV/PBS/Ecoflex Blends

Blend	Tensile St. (Mpa)	Un-notched Izod KJ/M^2
PHBV	35	6.5
PHBV/Ecoflex(70/30)	24	8.6
PHBV/Ecoflex(50/50)	15	25
PHBV/Ecoflex/PBS(50/20/30)	25	85

Conclusions

- Bioplastics alone do not meet many of the requirements of the marketplace

- Additives to improve heat performance and impact resistance of PLA are being developed

- Some progress being made in barrier coatings for PLA to improved barrier performance

- Blends of different Bioplastics are beginning to appear

- Copolymer solutions are limited to date