Mirel™ PHA Polymeric Modifiers & Additives

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Metabolix Core PHA Technology
Technology platform for bio-based polymers

**Biodegradable**
- Soil (Ambient)
- Home Compost
- Industrial Compost
- Fresh Water
- Marine Water
- Anaerobic

**Biobased**
Sugar used as feedstock

**Products**
PHA’s can be compounded and processed using conventional plastics processing equipment.

**Fermentation**
Microbial engineering enables high polymer accumulation in microbes.
Metabolix PHA Biopolymer Portfolio

**Key features**

- **100% Bio-based Polymers**
  - Made from renewable materials: industrial sugars & non-food plant oils

- **Copolyester chemistry**
  - MWt (200,000 - 700,000 gmol\(^{-1}\))
  - Semi-crystalline and amorphous structures
  - \(T_g\): -30 to +5°C, \(T_m\): 120 to 180°C

- **FDA food contact**: FCN1119 for PHA copolymers
  - Single use (conditions B through H)
  - In preparation for new copolymers (FDA, EFSA)

- **Biodegrade in most environments with microbial activity**
  - Hot to cold **aerobic** conditions: composting, soil, marine
  - Meso- & thermophilic **anaerobic**: high & low solids
Metabolix has Extended PHA Technology to Enable Amorphous PHA Grades

Metabolix PHA Family of Copolymers

![Graph showing the relationship between Tg (C) and % Crystallinity against mole % Comonomer with a highlighted amorphous range.](image-url)
Target Markets

Emphasis on Performance and Value as an Additive or Modifier

- **PLA modification** – 100% bio-based and compostable
- PVC modification
- Aqueous dispersion (latex)
- Micropowders for personal care products
Metabolix has Developed PLA / PHA Masterbatch Products Relative to Each Thermoplastic Process

<table>
<thead>
<tr>
<th>Converting Process</th>
<th>PLA Relative Viscosity</th>
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</thead>
<tbody>
<tr>
<td>Sheet/Profile/Clear Film <em>(high MW)</em></td>
<td>4.0</td>
</tr>
<tr>
<td>Inj. molding <em>(std flow)</em>, Foam, Film</td>
<td>3.3</td>
</tr>
<tr>
<td>Fibers (melt spun, spun bond non-wovens)</td>
<td>3.1</td>
</tr>
<tr>
<td>Inj. molding <em>(high flow)</em></td>
<td>2.5</td>
</tr>
<tr>
<td>Fibers (melt blown non-wovens)</td>
<td>2.5</td>
</tr>
</tbody>
</table>
Metabolix PHA Amorphous Modifiers

- Flexibility improvement is possible without lowering the Tg of the PLA (not a miscible plasticizer)
Metabolix PHA Amorphous Modifiers

- Increased Toughness of Injection Molded Products
Toughening PLA Sheet
*Dart impact improves with a-PHA modifier*

- Dart impact strength increase
- Reduced brittleness
- Improved ductility & elongation

Sheet thickness ~ 15 mil (0.37 mm)
Dart 1.5” hemisphere, 752 gm, 26” height

Dart Impact at different PHA %

Sheet thickness ~ 15 mil (0.37 mm)
Dart 1.5” hemisphere, 752 gm, 26” height

0%
5%
10% a-PHA

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PLA Sheet Trimming
Reduced brittle edge fracture

20x, without a-PHA
Crack propagation ahead of the cutting edge; splinters

20x, with 5% a-PHA
Rounded edges with reduced stress fracture & propagation

Refractive Indices

<table>
<thead>
<tr>
<th>Polymer</th>
<th>n_D^{25}</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA</td>
<td>1.48 – 1.49</td>
</tr>
<tr>
<td>a-PHA</td>
<td>1.48 – 1.49</td>
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</table>
PLA/PHA film has higher tensile yield strength like HDPE that enables greater load bearing & thinner gauges

<table>
<thead>
<tr>
<th></th>
<th>Units</th>
<th>LDPE** (typical)</th>
<th>PBAT/PLA*</th>
<th>PLA/a-PHA*</th>
<th>HDPE*** (typical)</th>
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</thead>
<tbody>
<tr>
<td>Melt index</td>
<td>g/10 min 2.16 kg @ 190°C</td>
<td>2.0</td>
<td>2.5</td>
<td>2.0</td>
<td>0.06</td>
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<tr>
<td>MD Tear</td>
<td>g/mil</td>
<td>350</td>
<td>250</td>
<td>200</td>
<td>11</td>
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<tr>
<td>Dart impact</td>
<td>g/mil</td>
<td>110</td>
<td>300</td>
<td>275</td>
<td>340</td>
</tr>
<tr>
<td>Tens. Yield</td>
<td>MPa</td>
<td>16</td>
<td>15</td>
<td>32</td>
<td>34</td>
</tr>
<tr>
<td>Tensile Modulus</td>
<td>MPa</td>
<td>183</td>
<td>445</td>
<td>1200</td>
<td>945</td>
</tr>
</tbody>
</table>

* Data of Metabolix 1.0 mil  
** Data of NA952-000 1.25mil LDPE from LyondellBasell  
*** Data of L5005 0.5 mil HDPE from LyondellBasell
PHA Modifiers Bring Significant Softness to PLA Fibers at Low Loading Level

- Addition of PHA in PLA tested in melt spun fibers, melt blown and spunbond non-wovens
- Incorporating PHA leads to improved fiber flexibility
- Flexibility & elongation lead to finer filaments & improved drape
- Reduction in “hand,” gives a soft, silky feel in woven and non-woven products
Target Markets

Emphasis on Performance and Value as an Additive or Modifier

- PLA modification – 100% bio-based and compostable
- PVC modification
  - Aqueous dispersion (latex)
  - Micropowders for personal care products
“Plastifier” - Flexible & Semi-rigid PVC
- High MW polymeric, soft amorphous modifier
- Excellent miscibility
- Improved permanence compared to primary plasticizers

Process Aid – Rigid and Recycled PVC
- Excellent miscibility – filler dispersion & fusion
- Lower process torque
- Improved dispersion, fusion & homogeneity of mixed PVC recycle streams
PHA Reduces Plasticizer Migration

Increasing a-PHA loading reduces conventional plasticizer migration.

ISO 177: Calculated plasticizer loss in 1 year at 70°C

**Weight Loss vs. Hardness**

- **DINP** – Conventional plasticizers
- **PHA** – Bio-based high MW polymeric modifier
- **ECR** – Synthetic polymeric modifier (*Ethylene Copolymer Resin*)
PHAs are Effective in Migration Reduction

- PHAs display similar performance to an ethylene copolymer resin (ECR)
  - lower migration response than conventional plasticizers
  - favorable impact on conventional plasticizer material performance

- PHA modifiers are inherently miscible in PVC
  
  \[ \text{More easily processed and incorporated than synthetics} \]

- PHAs are 100% bio-based and food-contact approved
  
  \[ \text{Increases bio-content, supports broad range of applications} \]
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Metabolix PHA Dispersion Technology

- Aqueous PHA dispersion (no VOCs)
  - No plasticizers or coalescing solvents

- Semi-crystalline PHA polymer resin
  - Polymer $T_m$: 160 to 180ºC, $T_g$: -5ºC

- High solids content (55%)
  - Viscosity range 300-550 cps
  - Dilutable without coagulation (no additional stabilizer)

- Particle size D50 1-2 microns
PHA Latex Solutions for Coated Paper and Cardboard

Metabolix aqueous PHA latex provides significant benefits:

– **Water and grease resistant coating** for paper/cardboard
– **Good heat sealability**: coating to coating, paper to coating
– **Allows repulping / recycling** of coated paper and cardboard
– Complements *inherent biodegradability* of paper and cardboard
Attributes in Coating or Modifying Paper

- **Coating performance (Tappi T441 0m-04)**
  - 50# Kraft & cup stock at ~20 g/m² coat weight
  - 30 min **Cobb results 5-20 g/m²** moisture gain
  - Variables include paper quality, drying and annealing conditions

- **Grease Resistance (Kit Test – Scale 0-12, 12 Good)**
  - Tappi value of ~10 flat (T 559 cm-12)
  - Tappi value of ~5-9 folded (T 465 sp-10)

- **Repulping**
  - Western Michigan University tests show 97% repulpability
  - Residual PHA is biodegradable in wastewater
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- **Micropowders for personal care products**
Properties of PHA Micropowders
Particle Size, Structure & Hardness

- Particle sizes can be tailored to the application
  - Ground micropowder D50 from 10-500 µm

- PHA hardness - from harder/more crystalline to softer
  
  **Harder** (Shore D: 78) - INCI registered
  - ~60% crystallinity

  **Softer** (Shore D: 59) - INCI registered
  - ~25% crystallinity
Mirel™ PHAs Biodegrade Rapidly in Active Microbial Marine Environments

ASTM D7081 Standard Specification requires > 30% biodegradation at 180 days
- Mirel PHA films achieved >30% biodegradation in 2 days
- At 13 days, Mirel PHA had exceeded 80% biodegradation, similar to cellulose
- Without microbial activity, PHA will not biodegrade even in aqueous formulations
PHA Micropowders
For use in cosmetic and personal care products

- Micropowders are common in personal care, oral care, beauty products, inks & adhesives

- Marine degradable PHA are replacements for non-degradable PE & synthetic wax powders
  - Demonstrated PHA marine biodegradability (independently certified) in fresh and marine saltwater/ocean environments
  - Heavier than water (non-floating). Promotes higher rate of biodegradation in sediment.

- Broad formulation compatibility
  - 100% bio-based (renewable feed-stocks)
  - Compatible with commonly used colorants
  - More versatile than other natural materials (e.g. walnut shells)
PHAs are Effective Performance Additives in a Range of Applications

- 100% bio-based & biodegradable
- PHA range includes unique amorphous PHA technology
- Effective in improving flexibility & toughness in brittle polymers, e.g. PLA & PVC
- New coatings & micropowders technology advancing

Thank You
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