Modification of PVC with Bio-based PHA Rubber

Yelena Kann, PhD
The first part of presentation on PHA modified flexible and semi-rigid PVC was given at the SPE Vinyltec October 2012.

Main conclusions:
- A step change in toughening, plasticization and processing improvement
- Improved environmental image with reduced additive usage levels, reduced additive migration, and renewable sourcing
- A platform for renewed innovation in PVC formulation

This presentation:
- More supporting data (weathering, fungi resistance, biodegradation, thermal stability)
- Additional data on rigid PVC impact modification
**Bio-Industrial Evolution**

Through bioscience and engineering, we bring clean, sustainable, and economically viable solutions to the world in plastics, chemicals, and energy.
Metabolix Core Capabilities
Industrial Biotechnology Leader – Two Primary Pathways

PHAs: Nature’s Versatile Family of Storage Materials

Fermentation

Industrial Crops

Two Primary Pathways
Efficient Recovery Process

Metabolic Engineering
Multi-gene Expression
Analytical Expertise
Process Engineering
Polymer Science & Product Dev.
Over 500 Patents Issued & Pending

Integrated Value Chain based on Metabolix PHA Core Competency
PHA Copolymers

Proprietary blend of random copolymers of poly(3-hydroxybutyrate)

Rigid

- Glass temperature: 10 °C
- Melting temperature: 180 °C
- Young’s modulus: 2.5 GPa
- Elongation at break: 3 %

Flexible

- Glass temperature: -50 °C
- Melting temperature: 60 °C
- Young’s modulus: 0.2 GPa
- Elongation at break: 1000 %
PVC Limitations

- **Flexible PVC**
  - Plasticizer migration
  - Volatile loss
  - Poor oil, fuel & solvent resistance; Staining
  - Difficulty handling viscous polymeric plasticizers

- **Rigid, semi-rigid and flexible PVC**
  - Low impact strength
  - Weathering and oxidative stability; Discoloration
  - Poor low temperature performance: brittleness and loss of flexibility
  - Poor PVC melting, fluxing, gloss
  - Poor thermal stability
  - Improvement of the tear resistance, abrasion resistance, compression set, flex modulus are always of interest
Van Krevelen Solubility Parameters

<table>
<thead>
<tr>
<th></th>
<th>Total</th>
<th>Polar</th>
<th>Non-polar</th>
</tr>
</thead>
<tbody>
<tr>
<td>vinyl chloride</td>
<td>21.2</td>
<td>24.1</td>
<td>16.1</td>
</tr>
<tr>
<td>3-hydroxybutyrate</td>
<td>20.4</td>
<td>27.3</td>
<td>17.1</td>
</tr>
<tr>
<td>4-hydroxybutyrate</td>
<td>19.8</td>
<td>27.3</td>
<td>16.1</td>
</tr>
<tr>
<td>3-hydroxyvalerate</td>
<td>19.6</td>
<td>27.3</td>
<td>16.9</td>
</tr>
<tr>
<td>methyl methacrylate</td>
<td>19.5</td>
<td>27.3</td>
<td>16.7</td>
</tr>
<tr>
<td>DIDP plasticizer</td>
<td>17.6</td>
<td>27.3</td>
<td>16.3</td>
</tr>
</tbody>
</table>

Preformed butadiene/MMA, butyl acrylate/MMA particles:

Interpenetrating networks
PU/PMMA, PVC/ENR

Ref. Polymer blends and alloys, ed. G. Shonaike, Marcel Dekker Inc., 1999
PVC/PHA Miscibility

Unplasticized PVC/28 phr PHA blend

Plasticized PVC/15 phr PHA blend

Phase morphology
PVC/PHA Miscibility

- DMA tg δ as a function of temperature (with 18 phr DIDP):

Fox equation confirmed miscibility

\[
\frac{1}{T_{gb}} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}}
\]
PVC/PHA Miscibility, continued

Unplasticized PVC with 28 phr PHA

Multi frequency DMA

Fox equation (confirmed miscibility):

Good molecular adhesion: small damping at Tg
Physical Properties – Semi-rigid PVC/PHA Blends

Flex modulus, MPa

Notched impact, Izod, ft lb/inch

Hardness, shore D
Physical Properties – Flexible PVC/PHA Blends

**Tensile Toughness, J**

- 5 phr Acrylic proc. Aid, 36 phr DIDP
- 5 phr m-pact I6002, 36 phr DIDP
- 15 phr m-pact I6002, 25 phr DIDP

**Tear, N/mm**

- 5 phr Acrylic proc. Aid, 36 phr DIDP
- 5 phr m-pact I6002, 36 phr DIDP
- 15 phr m-pact I6002, 25 phr DIDP

**Hardness, Shore D**

- 5 phr Acrylic proc. Aid, 36 phr DIDP
- 5 phr m-pact I6002, 36 phr DIDP
- 15 phr m-pact I6002, 25 phr DIDP
Fungal Resistance, ASTM G21-09
(28 days at 28-30 °C and ≥85% relative humidity)

PVC control: 1 out of 3 samples trace of growth

PVC+15phr PHA: 3 out of 3 samples no growth. Fungal resistance!

Viability control
Soil Disintegration
(20-23 °C MA farm soil, 10-12% moisture)

Weight loss data, g

<table>
<thead>
<tr>
<th></th>
<th>2 weeks</th>
<th>4 weeks</th>
<th>8 weeks</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC</td>
<td>-0.03</td>
<td>0.02</td>
<td>0.14</td>
</tr>
<tr>
<td>PVC=100 phr, I6001=15 phr</td>
<td>-0.02</td>
<td>-0.14</td>
<td>0.03</td>
</tr>
<tr>
<td>PVC=100 phr, ASA impact modifier=15 phr</td>
<td>0.15</td>
<td>-1.49</td>
<td>0.15</td>
</tr>
<tr>
<td>PVC=100 phr, I6001=15 phr, DINA=18 phr</td>
<td>0.33</td>
<td>0.42</td>
<td>0.75</td>
</tr>
<tr>
<td>I6001</td>
<td>2.46</td>
<td>8.85</td>
<td>35.98</td>
</tr>
</tbody>
</table>
### Xenon Weathering, Plasticized PVC Compounds
(18 phr DINA) Tested per ASTM G155-2005

<table>
<thead>
<tr>
<th>I6001</th>
<th>250 kJ</th>
<th>750 kJ</th>
<th>1250 kJ</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC=100 phr, I6001=15 phr, ESO =4.5 phr, BaZn stab. =4 phr, DINA=18 phr</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVC=100 phr, ABS imp. modifier=15 phr, ESO=4.5 phr, BaZn stab.=4phr, DINA=18 phr</td>
<td></td>
<td></td>
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<td>PVC=100 phr, ASA imp. modifier=15 phr, ESO=4.5 phr, Ba Zn stab.=4phr, DINA=18 phr</td>
<td></td>
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<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>DL*</th>
<th>Da*</th>
<th>Db*</th>
<th>DE*</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC +18 phr DINA+ 15 phr PHA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>250 kJ</td>
<td>-0.51</td>
<td>-0.30</td>
<td>0.62</td>
</tr>
<tr>
<td>750 kJ</td>
<td>-0.70</td>
<td>-0.01</td>
<td>-1.37</td>
</tr>
<tr>
<td>1250 kJ</td>
<td>0.82</td>
<td>0.01</td>
<td>-1.92</td>
</tr>
</tbody>
</table>

| PVC +18 phr DINA+ 15 phr ABS |
| 250 kJ | -1.11 | -0.97 | 6.78 | 6.94 |
| 750 kJ | -2.04 | -1.03 | 7.76 | 8.09 |
| 1250 kJ | -4.20 | -1.12 | 7.90 | 9.02 |

| PVC +18 phr DINA+ 15 phr ASA |
| 250 kJ | 0.08 | -2.07 | -2.94 | 3.60 |
| 750 kJ | 0.42 | -2.39 | -2.58 | 3.54 |
Xenon Weathering, cont.
FDA Approval

Metabolix polymeric modifier I6001 is the subject of US FDA Food Contact Notification (FCN) 001119, which became effective on January 21, 2012 and is listed in the Inventory of Effective Food Contact Substance (FCS) Notifications:

http://www.accessdata.fda.gov/scripts/fcn/fcnDetailNavigation.cfm?rpt=fcsListing&id=1119

Per FCN 001119, I6001 can be used as a polymer that may contact all food except alcoholic food under Conditions of Use B through H \(^{(1)}\).
Hardness Modification and Rheology

No thermal degradation with PHA
Slight MW preservation

Improved melt strength compared to MBS core-shell blends
Kissinger equation for $E_{act}$:

$$\beta \frac{E_a}{R T_m^2} = A_n (1 - \alpha)_m^{n-1} \exp \left(-\frac{E_a}{RT_m}\right)$$

where $\alpha$ - conversion; $E_a$ - apparent activation energy, kJ/mol; $A_n$ – pre-exponential factor; $\beta$ – heating rate, °C/min; $R$ - general gas constant, J/mol °K; $T_m$- temperature at maximum degradation rate, °K; $n$ - reaction order

<table>
<thead>
<tr>
<th>Type of sample</th>
<th>$E_{act1}$, kJ/mol</th>
<th>$E_{act2}$, kJ/mol</th>
<th>T5% loss, °C</th>
<th>$T_m1$, °C</th>
<th>$T_m2$, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC control, 18 pphr DIDP</td>
<td>116.3</td>
<td>252.7</td>
<td>287.7</td>
<td>304.5</td>
<td>457</td>
</tr>
<tr>
<td>PVC/10phr PHA, 18 phr DIDP</td>
<td>115.7</td>
<td>287.2</td>
<td>280</td>
<td>308</td>
<td>463</td>
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</table>
PVC/PHA Blends
Thermal Degradation, cont

No significant effect of PHA on thermal degradation of PVC: both plasticized and not:

Mw GPC data:

<table>
<thead>
<tr>
<th>phr PHA</th>
<th>Mw, PVC, g/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>60,246</td>
</tr>
<tr>
<td>5</td>
<td>63,254</td>
</tr>
<tr>
<td>15</td>
<td>64,326</td>
</tr>
<tr>
<td>28</td>
<td>58,953</td>
</tr>
</tbody>
</table>
New modifications of PHA for RIGID PVC

Goal: High impact and stiffness

<table>
<thead>
<tr>
<th></th>
<th>ASA imp. modif.=15 phr</th>
<th>MBS imp. modif.=15 phr</th>
<th>ABS imp. modif.=15 phr</th>
<th>CPE imp. modif.=15 phr</th>
<th>Next generation PHA, 15 phr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Notched Izod, ft lb/inch</td>
<td>2.2</td>
<td>15.5</td>
<td>17.4</td>
<td>2.57</td>
<td>5.39</td>
</tr>
<tr>
<td>Flex modulus, MPa</td>
<td>2181</td>
<td>2300</td>
<td>2490</td>
<td>1369</td>
<td>2488</td>
</tr>
</tbody>
</table>

Very promising! Still under development
New modifications of PHA for RIGID PVC

![Graph](https://via.placeholder.com/150)

- Storage Modulus (MPa)
- Temperature (°C)

Materials:
- 44.001 ASA
- 72.001 ABS
- A1.001 CPE
- A3.001 New PHA
- 49.001 MBS

Instrument: Universal V3.9A TA Instruments
New modifications of PHA for RIGID PVC

![Graph showing Tan Delta values against Temperature (°C) for different materials, including ASA, ABS, CPE, new PHA, and MBS.](image-url)
PHAR Polymeric Modifiers have Wide Potential Application

<table>
<thead>
<tr>
<th>PVC drawbacks</th>
<th>PHA contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brittleness and loss of flexibility; poor low temperature performance</td>
<td>Effective polymeric plasticization and impact modification in a single additive solution. Ability to reduce overall use of modifiers.</td>
</tr>
<tr>
<td>Poor melting, fluxing, gloss</td>
<td>Improved melting and flow promotion</td>
</tr>
<tr>
<td>Plasticizer migration. Volatile loss. Poor oil/fuel/solvent resistance, staining. Safety concerns with phthalates</td>
<td>Polymeric plasticization inhibits migration. Inherent polyester chemical resistance Reduced overall use of migratory plasticizers</td>
</tr>
<tr>
<td>Feeding &amp; handling issues with viscous polymeric plasticizers</td>
<td>Easy to handle easy flowing pellets</td>
</tr>
<tr>
<td>UV instability and Discoloration from additives</td>
<td>Inherent UV stability PVC miscibility protecting transparency. Ability to reduce overall use of stabilizers.</td>
</tr>
</tbody>
</table>