FUNCTIONAL POLYOLEFINS

Maleated polyolefins as versatile HFFR coupling agents

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R&D Center
Summary

ARKEMA at glance

HFFR compounds in cable

Case study:
- Brucite based compound
- NEW OREVAC® 18341 for better compound properties

Conclusion
Arkema in a snapshot

- Global producer of specialty chemicals
- Sales of €6.1 bn*
- Worldwide n°1 to n°3 on 90% of our portfolio
- 14,000 employees in 40 countries
- 90 industrial plants
- 10 research centers
- 3 Business segments:
  - High Performance Materials
  - Industrial Specialties
  - Coating Solutions

Sales by segment*

Sales by region*

* 2013 figures
Innovation is the heart of Arkema’s strategy

10 research centers
≈€150 m allocated to R&D
1,200 researchers
HFFR compounds in cables

- HFFR cables sheathing are growing thanks to very low smoke release properties
- HFFR cables are pushed by regulation (CPR,....)
- HFFR cables face PVC competition

PVC cables:
- 30 seconds
- 3 minutes
- 6 minutes

HFFR cables:
HFFR growth in W&C will induce:

- Increase of technical requirement (cables air and water ageing, mechanical properties)
- Price gap decrease with PVC to further develop the market
HFFR compounds typical components

Ethylene copolymer + Mineral filler + Coupling agent

- Filler acceptance/ Flexibility
- Flame Retardancy
- Cohesion / Mechanical properties

Main polyolefins:
- Ethylene copolymers (EVA, EMA, EBA)
- Polyethylene (VLD,LD, LL, HD), Polypropylene
- Coupling agents: maleated polyolefins
Main Polymers in HFFR

Copolymers

- Ethylene – Vinyl Acetate
- Ethylene – Alkyl Acrylate

Terpolymers → Ethylene – Alkyl Acrylate – MAH/GMA

Copolymers

Ethylene copolymer matrix

Coupling agent

PE (LD, LLD, HD)  PP  EVA

Grafted Polyolefins → MAH - Grafted

Arkema
EMA/EBA/EVA vs. PE: Fire properties

Better LOI with Evatane® or Lotryl® resins compared to all kind of PE
Introduce +/- 65% of mineral filler to match PVC LOI

*LOI: Limiting Oxygen Index
= minimum amount of oxygen in atmosphere to maintain combustion
Role of coupling agents

Coupling Agent = THE link between filler (sand-like) and polymer
⇒ Mechanical properties improvement

Specific link for the 65% mineral filler with the polymer matrix is mandatory

Most of the mineral fillers for HFFR have hydroxyl functions available:

- Aluminium hydroxide (precipitated ATH)
- Magnesium hydroxide (precipitated MDH)
- Brucite (Natural ground MDH)
- ....

**High content MAH** grafted polymers or MAH Terpolymers, reactive in presence of hydroxyl function, can play as coupling agent
**Lotader®**: MAH –based Reactive Polyolefins (Terpolymers)

*Ethylene – Acrylic Ester – Maleic Anhydride (MAH)*

\[
\begin{align*}
(\text{CH}_2 - \text{CH}_2 -)_x & \quad (\text{CH}_2 - \text{CH}_2 -)_y & \quad (\text{CH}_2 - \text{CH}_2 -)_z & \quad (\text{CH} - \text{CH} -)_t \\
\text{R=} & \text{Methyl CH}_3, \text{Ethyl C}_2\text{H}_5, \text{Butyl C}_4\text{H}_9
\end{align*}
\]

*Ethylene – Acrylic Ester* + *Maleic Anhydride*

- **Compatibility with the base polymer** (EVA, EMA, EBA, PE)
- A bond is formed by reaction between MAH and hydroxyl groups present of the filler
- Good efficiency with both ATH and MDH

**Coupling agents**: maleated copolymers

**Ethylene copolymer** + **Filler** + **Coupling agent**
**Coupling agents: MAH-grafted copolymers**

**Orevac®**: MAH based Reactive Polyolefins (Grafted Polyolefins)

*Ethylene –Grafted Maleic Anhydride (MAH)*

Broad choice of grafted polymer:
- HDPE, LLDPE, VLDPE.

Grafted Maleic Anhydride key features in HFFR:
- Plays a key role in the mechanical properties
- Gives polarity and high reactivity to polymer chains ➔ Higher filler acceptance
- Strongly interacts with OH (hydroxyl) of mineral filler (ATH, MDH,..)
- Enables large processing window thanks polymer choice

**Ethylene copolymer**
+ **Filler**
+ **Coupling agent**

High reactivity of GRAFTED MAH
Role of coupling agents

Coupling Agents improve mechanical properties
Elongation ↑++ , Tensile strength ↑+

Without Coupling Agent

With 5% of Grafted LLDPE Orevac® 18341

Ethylene copolymer + Filler + Coupling agent

Effect of a Coupling Agent
Coupling Agents improve mechanical properties
Elongation ↑++, Tensile strength ↑+

Ethylene copolymer + Filler + Coupling agent

With 5% of Grafted LLDPE Orevac® 18341

Orevac® by Arkema

AMI Cables 2015 Cologne
Case study: Brucite as mineral filler

Hydrated mineral filler is more than 60% of the recipe.

Natural ground product like brucite (natural MDH) is of interest.

Main issue known with brucite is to obtain good mechanical, good FR(LOI) and not too viscous compound.

Key properties to succeed with brucite are purity and size distribution.
Case study: Brucite as mineral filler

Formulation & test method

Internal mixer

Roll calender

Hot press compression

Mineral filler cross-check
Goal 63%(+/-1)

Mechanical/LOI/MFI
Case study: Brucite as mineral filler

Technical request:

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>Tensile strength (TS)</td>
<td>≥ 10 MPa</td>
</tr>
<tr>
<td>Elongation @ break (EB)</td>
<td>≥ 140%</td>
</tr>
<tr>
<td>LOI</td>
<td>≥ 34%</td>
</tr>
<tr>
<td>MFI (150°C/21.6kg)</td>
<td>≥ 2.5</td>
</tr>
</tbody>
</table>
Case study: Brucite as mineral filler

- ARKEMA approach for this new HFFR compound is to start from our knowledge e.g. in formulation

<table>
<thead>
<tr>
<th>Product</th>
<th>%wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>EVA / EMA / EBA</td>
<td>23</td>
</tr>
<tr>
<td>PE (LD, HD, LL, VLD)</td>
<td>9</td>
</tr>
<tr>
<td>Maleated polyolefins</td>
<td>5</td>
</tr>
<tr>
<td>Lotader®/Orevac® resins</td>
<td></td>
</tr>
<tr>
<td>Mineral flame retardant filler</td>
<td>63</td>
</tr>
<tr>
<td>Al(OH)3 or Mg( OH)2</td>
<td></td>
</tr>
<tr>
<td>Stabilizer, processing aid</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

Goal
- Identify the difference induced on the compound by replacing precipitated ATH (63%) by ground brucite (63%)
Case study: Brucite as mineral filler

Mechanical properties: Tensile & Elongation

Tensile Strength @break (Mpa)
Brucite vs p-ATH

Elongation @break (%)
Brucite vs p-ATH
Case study: Brucite as mineral filler

MFI & LOI:

- Ground brucite highly viscous
- LOTADER® 3210 dramatically reduces viscosity

![Graph showing LOI and MFI for Brucite vs ATH with 2 coupling agents]
Case study: Brucite as mineral filler

With standard recipe unsufficient coupling between natural MDH and EVA/PE polymer matrix.

- Viscosity => MFI to be increased without reducing other properties
- Elongation at break => to be increased

We should play on both directions:

- Replace LLDPE by VLDPE to increase the mechanicals while keeping the coupling agent at same level
- Introduce EVATANE® 28-800 (VA 28%, MFI 800) very high fluidity EVA to reduce the compound viscosity

NOTA: working in a sole way (VLDPE usage or fluid EVA usage) would lead to unbalanced compound properties.
### Brucite as mineral filler: Phase II recipe

<table>
<thead>
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<tbody>
<tr>
<td>EVATANE® 28-03</td>
<td>23</td>
</tr>
<tr>
<td>EVATANE® 28-800</td>
<td>2</td>
</tr>
<tr>
<td>PE-g-MAH OREVAC®</td>
<td>5</td>
</tr>
<tr>
<td>VLDPE</td>
<td>7</td>
</tr>
<tr>
<td>Brucite</td>
<td>63</td>
</tr>
<tr>
<td>Stabilizer, processing aid</td>
<td>&lt;1</td>
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Brucite as mineral filler: Phase II mechanical

Mechanical properties: Tensile & Elongation

VLDPE and EVATANE® 28-800 increase coupling efficiency
Brucite as mineral filler: Phase II

**MFI & LOI**

**VLDPE & EVATANE®**
28-800 decrease viscosity (MFI x2)

Graph: LOI and MFI Brucite vs ATH
### Brucite as mineral filler: Conclusion

This specific recipe meets requirement (TS>10MPa, EB>140%)

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Case study Nr2: MAH level and properties

Maleated coupling agent:
- Commercial polymer (PE, PP, EVA,...)
- Maleic Anhydride (MAH) grafted or terpolymers

Polymer selected to match the polymer matrix
%MAH and his influence?
**MAH level and properties: PE-g-MAH comparison**

- **LLDPE-g-MAH medium grafted**: Recipe A
- **LLDPE-g-MAH highly grafted (reference)**: Recipe B
- **OREVAC® 18341 highly grafted**: Recipe C

<table>
<thead>
<tr>
<th>RECIPE A</th>
<th>%wt</th>
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<tbody>
<tr>
<td>EVATANE® 28-03</td>
<td>23</td>
</tr>
<tr>
<td>LLDPE</td>
<td>9</td>
</tr>
<tr>
<td>LLDPE-g-MAH medium</td>
<td>5</td>
</tr>
<tr>
<td>ATH</td>
<td>63</td>
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</table>

<table>
<thead>
<tr>
<th>RECIPE B</th>
<th>%wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>EVATANE® 28-03</td>
<td>23</td>
</tr>
<tr>
<td>LLDPE</td>
<td>9</td>
</tr>
<tr>
<td>LLDPE-g-MAH High</td>
<td>5</td>
</tr>
<tr>
<td>ATH</td>
<td>63</td>
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</table>

<table>
<thead>
<tr>
<th>RECIPE C</th>
<th>%wt</th>
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<tbody>
<tr>
<td>EVATANE® 28-03</td>
<td>23</td>
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<tr>
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<td>OREVAC® 18341</td>
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<tr>
<td>ATH</td>
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MAH level and properties: PE-g-MAH comparison

- LLDPE-g-MAH medium grafted: Recipe A
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<thead>
<tr>
<th>RECIPE A</th>
<th>RECIPE B</th>
<th>RECIPE C</th>
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<tbody>
<tr>
<td><strong>Tensile strength</strong></td>
<td><strong>11</strong></td>
<td><strong>Tensile strength</strong></td>
</tr>
<tr>
<td><strong>Elong. @ break</strong></td>
<td><strong>195</strong></td>
<td><strong>Elong. @ break</strong></td>
</tr>
<tr>
<td><strong>MFI(150°/21.6kg)</strong></td>
<td><strong>3,3</strong></td>
<td><strong>MFI(150°/21.6kg)</strong></td>
</tr>
<tr>
<td><strong>LOI</strong></td>
<td><strong>38</strong></td>
<td><strong>LOI</strong></td>
</tr>
<tr>
<td><strong>Water Resistance</strong></td>
<td><strong>Fail</strong></td>
<td><strong>Water Resistance</strong></td>
</tr>
</tbody>
</table>

Water aging: 7days 70°C; variation <40%, TS>9Mpa, EB >100%
**MAH level & properties: highly grafted & Terpolymers**

- LLDPE-g-MAH highly grafted (reference): Recipe B
- **OREVAC® 18341 3%** highly grafted: Recipe D
- **OREVAC® 18341 2,5% + LOTADER® 2,5%**: Recipe E

<table>
<thead>
<tr>
<th>RECIPE B %wt</th>
<th>RECIPE D %wt</th>
<th>RECIPE E %wt</th>
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<tbody>
<tr>
<td><strong>EVATANE® 28-03</strong> 23</td>
<td><strong>EVATANE® 28-03</strong> 25</td>
<td><strong>EVATANE® 28-03</strong> 23</td>
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<tr>
<td>LLDPE 9</td>
<td>LLDPE 9</td>
<td>LLDPE 9</td>
</tr>
<tr>
<td>LLDPEg-MAH High 5</td>
<td><strong>OREVAC® 18341</strong> 3</td>
<td><strong>OREVAC® 18341</strong> 2,5</td>
</tr>
<tr>
<td><strong>LOTADER® 3210</strong> 2,5</td>
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<td><strong>LOTADER® 3210</strong> 2,5</td>
</tr>
<tr>
<td>ATH 63</td>
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**MAH level & properties: highly grafted & Terpolymers**

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<th>Tensile strength</th>
<th>Elong. @ break</th>
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<th>LOI</th>
<th>Water Resistance</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>14</td>
<td>185</td>
<td>3,7</td>
<td>38</td>
<td>Pass</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>RECIPE D</th>
<th>Tensile strength</th>
<th>Elong. @ break</th>
<th>MFI(150°/21.6kg)</th>
<th>LOI</th>
<th>Water Resistance</th>
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<tbody>
<tr>
<td></td>
<td>14</td>
<td>200</td>
<td>6</td>
<td>38</td>
<td>Pass</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>RECIPE E</th>
<th>Tensile strength</th>
<th>Elong. @ break</th>
<th>MFI(150°/21.6kg)</th>
<th>LOI</th>
<th>Water Resistance</th>
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Water aging: 7days 70°C; variation <40%, TS>9Mpa, EB >100%
Water aging: highly grafted & Terpolymers

Elongation @ break % and variation

Water aging: 7 days 70°C; variation <40%, TS>9Mpa, EB >100%
Water aging: highly grafted & Terpolymers

Water aging: 7days 70°C; variation <40%, TS>9Mpa, EB >100%
OREVAC® 18341 alone at different %wt pass the requirement and offer good performance/cost ratio.

OREVAC® 18341 + LOTADER® 3210 is a solution for stringent technical request.
NEW OREVAC® 18341
Versatile coupling agent
Good combination of elongation at break and tensile strength
⇒ Building HFFR cables

OREVAC® 18507 HDPE based
Higher resistance to chemical and abrasion
Good temperature stability
⇒ XL Automotive HFFR Cables

OREVAC® OE808 VLD/LLDPE
Flexibility at low temperature while maintaining high temperature performance
⇒ Soft cables, high-end HFFR

LOTADER® 3210 Terpolymer BA/MAH
Low melting Temperature
⇒ low mixing Temperature internal mixer
Low viscosity, good water resistance
⇒ Blend in OREVAC® resins

OREVAC® 18302N LLDPE based
High Elongation at break

OREVAC® CA100 HOMO PP based
For PP-based HFFR formulations
⇒ higher Temperature MDH compounds without cross linking
Acknowledgements to: Dr Sébastien QUINEBECHE, Elisabeth LOERCH, Dominique BAILLEUL among others ARKEMA CERDATO colleagues.

Thank you for your kind attention

More information:

www.evatane.com
www.lotryl.com
www.lotader.com
www.orevac.com