Polyolefin innovations & new catalyst systems

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12th Saudi-Japan Symposium
15 & 16 December 2002
The Research Institute Dhahran, Saudi Arabia
Topics

- State-of-the-art: why change?
- Basell and *Avant* catalysts
- Phthalate catalysts - evolution
- Diether/Succinates catalysts - revolution
- Catalyst selection
- PE 100 pipe grades
- Conclusions
Why change catalysts?

**Risks**
- Operational problems
- Time / resources needed for trials
- Dispose of non-standard products
- Customer re-qualifications
- Loss of existing business

**Rewards**
- Expand product capability
- Expand capacity
- Generate new business
- Better plant operability
- Improve economics
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Our key strength is **process** and **catalyst** integration

- **Avant ZN** | Ziegler Natta PP
- **Avant Z** | Ziegler PE
- **Avant C** | Chromium PE
- **Avant M** | Metalloocene PP
Basic principles of *Avant* ZN catalysts

**Catalyst manufacture**

1. **Base Support**
   - $\text{MgCl}_2$
   - Alcohol

2. **Titanation**
   - $\text{TiCl}_4$
   - Internal donor

3. **Avant ZN Catalyst**
Basic principles of Avant ZN catalysts - role of internal donor

With the internal donor, it is possible to modulate:

- Catalyst Activity
- Stereocontrol
- Hydrogen Response

- Polymer MW & MWD
- Microtacticity
- Oligomers Content

\[\downarrow\] improvement of the polymerisation process

\[\downarrow\] improvement/tailoring of polymer mechanical and rheological properties
PP manufacture

1. Avant ZN Catalyst

2. Activation
   - aluminum alkyl
   - external donor

3. Polymerization
   - propylene

4. PP products
**Avant ZN Range - 35 Catalysts to choose from!**

<table>
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<th>Spheripol</th>
<th>Slurry</th>
<th>LIPP</th>
<th>Bulk +</th>
<th>Gas Phase</th>
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</tbody>
</table>

‡ - Under development / * - Not applicable for this technology
Catalyst requirements for different process technologies

1st considerations
- Activity profiles
- Morphology
- Porosity

2nd considerations
- Yield (mileage)
- Stereo-regularity
- Hydrogen response
- Bulk density
- External donor
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What is a **phthalate** catalyst?

- 4th generation
- uses **phthalates** as internal donor
- good morphological control
- multi-purpose catalyst
- general applications
Avant ZN Series Catalysts - drop-in product capability

ZN111 Catalyst vs Traditional Catalyst
H2 Response

- ▲ ZN111 Catalyst
- ■ Traditional 4th Gen. Catalyst

<table>
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<tr>
<th>H2 concentration (ppm)</th>
<th>MFR (g/10 min)</th>
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<tr>
<td>1000</td>
<td>10</td>
</tr>
<tr>
<td>10000</td>
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</table>
ZN111 Catalyst vs. Traditional 4th Generation Catalyst
Yield - MFR Response

- ZN111 Catalyst
- Traditional 4th Gen. Catalyst
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- **Diether/Succinates catalysts** - revolution
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What is a **diether** catalyst?

- 5th generation
- uses **diethers** as internal donor
- benzene free
- high mileage
- H2 control
- narrow MWD
- SB & MB fibres, TWIM, high stiffness IM
Diether Catalysts - even higher polymerisation activity

Diether Catalyst vs Traditional Catalysts
Yield/Melt Flow Response

- Diether
- Diether + D-Donor
- ZN111
- Traditional 4th Gen. Catalysts

Yield (kg/g) vs MFR (g/10 min)
Diether Catalysts - reaching ever higher isotacticity levels

Diether Catalyst vs. Traditional Catalyst
MFR vs. Xylene Insolubles

- Diether
- Diether + D-donor
- Traditional 4th Gen. Catalyst
Polyolefin innovations & new catalyst systems

Avant ZN **diether** catalysts - high MFR from the reactor

**Avant** ZN diether vs Traditional 4th Generation catalyst
H2 Response

- ▲ Diether Catalyst
- ■ Traditional 4th Gen. Catalyst

MFR (g/10 min) vs H2 concentration (ppm)
Avant ZN diether catalysts - non woven applications
Avant ZN diether catalysts - Melt Blown Fibres

Uniform fibre thickness distribution

Conventional catalyst

Diether catalyst
Avant ZN diether catalysts - TWIM applications

- High flow
- Faster molding & lower thickness improving productivity and cost
- Superior impact-stiffness balance
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- *Avant* Z 501 catalyst for PE 100 pipe grades
- Conclusions
What is a **succinate** catalyst?

- 5th generation
- uses **succinates** as internal donor
- benzene free
- broad MWD
- BOPP, pipes, injection molding
Homopolymers

- High isotacticity with broad MWD
- High stiffness injection molding grades
- Pipes with improved processability & physical properties
- BOPP improved cost / performance

Copolymers

- High stiffness / impact injection molding applications
Succinate Catalysts - superior HeCo balance

Succinate Catalyst vs. Traditional Catalysts
Un-nucleated HeCo Impact/Stiffness Balance

- Succinate/D (monomodal)
- Phthalate/D (monomodal)
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Avant ZN catalyst selection - homopolymers

Polydispersity Index

Isotacticity (Xt)

99 %

98 %

97 %

96 %

3.0 4.0 5.0 6.0 7.0 8.0

Diether Phthalate Succinate

Multi-modal Process Capability

Multi-modal Process Capability

Succinate

Phthalate

Diether
Avant ZN catalyst selection - copolymers

Polydispersity Index

- Diether
- Phthalate
- Succinate

Ethylene Content

- 0%
- 10%
- 20%
- 30%

Multi-modal Process Capability

Polyolefin innovations & new catalyst systems
If new catalysts are to be successful, it is essential to have a thorough understanding of the process and the products, as well as the catalyst.

There are risks in changing catalysts, but there may also be rewards.

The evolution of existing phthalate catalysts is still ongoing, and will continue to play an important role in the future.

The use of new revolutionary internal donors, such as diethers and succinates, enhance the capabilities of the catalysts.

Basell has multiple Avant ZN PP catalysts suitable for bulk, slurry and gas phase processes.

Basell is uniquely positioned as the leading catalyst supplier, process licensor and PP manufacturer to generate and successfully commercialise new innovations.
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◆ Conclusions
Tailoring of product properties
by
tailoring of molecular mass distribution and comonomer distribution

- very low molecular mass
- homopolymer
- high crystallinity
  ➔ processability
  ➔ stiffness

- very high molecular mass
- copolymer
- low crystallinity
  ➔ impact strength
  ➔ stress crack resistance

- broad molecular mass distribution
- inverse comonomer distribution
  ➔ melt flowability
  ➔ long time hydrostatic strength (pipe)
  ➔ strain hardening (film)
**ADVANTAGES:**

- higher stiffness (high modulus)
- higher toughness
- higher stress crack resistance (long life time under stress)
- higher resistance to rapid crack propagation
- better processability
- Hostalen CRP 100 is listed in the PE 100+ Association
State-of-the-art: why change?

Basell and *Avant* catalysts

Phthalate PP catalysts - evolution

Diether/Succinate PP catalysts - revolution

PP catalyst selection

*Avant Z 501* catalyst for PE 100 pipe grades

**Conclusions**
Conclusions

*Basell predecessor companies have played an important role in the evolution of the polyolefins industry through new catalyst and process developments.*

*We expect our new revolutionary systems will continue to shape the future of this industry.*

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Thank you for your attention

Polyolefin innovations:
The race continues

Thank you for your attention