Dieter Roland
Director
Comar Chemicals (Pty) Ltd

Superior Polybutadiene properties achieved with Breakthrough in Rare Earth Finished Catalyst Technology

Catalyst Systems for solution polymerization of Polybutadiene

- Ziegler-Natta catalysts developed in 1954 for polymerization of conjugated dienes
- Early 1960’s first systems Co or Ti based, then dominance of Ni-based BR
- Large-scale Nd-BR since early 1980’s
### Comparison of BR Catalyst systems

<table>
<thead>
<tr>
<th>Cobalt</th>
<th>Nickel</th>
<th>Neodymium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Branched</td>
<td>Intermediate branching</td>
<td>Highly Linear rubber - no branching</td>
</tr>
<tr>
<td>Low solution viscosity</td>
<td></td>
<td>Highest CIS content</td>
</tr>
<tr>
<td>Chain insertion : High PDI</td>
<td>Chain Transfer : high PDI</td>
<td>Superior tensile strength</td>
</tr>
<tr>
<td>ABS grade possible</td>
<td></td>
<td>Good abrasion resistance</td>
</tr>
<tr>
<td>Gel Variable</td>
<td>Gel medium</td>
<td>Gel Low</td>
</tr>
<tr>
<td>Cold Flow : Adjustable</td>
<td>Cold flow : low</td>
<td>Cold flow : high</td>
</tr>
<tr>
<td>Tg : -106 ° C</td>
<td>Tg : -107 ° C</td>
<td>Tg : -109 ° C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Difficult to process</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Long Carbon Black incorporation times</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Expensive catalyst system</td>
</tr>
</tbody>
</table>

**56th AGM * Future Vision.....Forward Movement **
Prevalence of BR Catalyst Systems in 2014

- Cobalt/Other: 5%
- Neodymium: 20%
- Nickel: 75%

High proportion of new BR plants utilize Nd catalysis

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Future Vision...Forward Movement

Current most common Nd Catalyst Technology

Homogeneous catalyst system comprising

1. Nd Catalyst: Neodymium Versatate (Nd-V₃ in hexane)

   Co-catalysts:

2. Alkylating Agent: Di-Butyl Aluminium Hydride (DiBAH)
3. Halide: Ethyl Aluminium Sesqui-Chloride (EASC)

<table>
<thead>
<tr>
<th>IN-SITU</th>
<th>PRE-FORM</th>
</tr>
</thead>
<tbody>
<tr>
<td>High catalyst &amp; co-catalyst usage</td>
<td>High activity</td>
</tr>
<tr>
<td>No catalyst stability issue</td>
<td>Catalyst complex ages with time – BR quality varies</td>
</tr>
</tbody>
</table>
Example of active Nd catalyst complex formation & polymerization

Pre-form Nd-BR – Catalyst Synthesis

Nd-V, DiBAH, EASC, Hexane

Catalyst Storage

Catalyst to BR reactor

Zichao, 2010, Springer
**Nd-BR Reactor**

- Adiabatic reaction
- $\Delta T = \text{up to } 120^\circ \text{C}$
- Residence time: 60 minutes
- Conversion: 100%

**In-situ Nd-BR Reactor**

- Adiabatic reaction
- $\Delta T = \text{up to } 120^\circ \text{C}$
- Residence time: 60 minutes
- Conversion: 100%
Key features of Standard Nd catalysts

- Multiple active sites
- Highly active species, short-lived, high MW rubber
- Unstable Pre-formed catalyst complex – catalyst ageing

All of the above leads to:

- Unsymmetrical rubber MW distribution
- Changing BR with catalyst age
- High PDI
- Lower Mn for any given Mooney
- Compromise in physical strength properties
- High solution viscosity
- Difficult and energy intensive rubber processing

Variation of BR MW distribution of standard Nd-catalysts with reaction time

![Graph showing MW distribution over time](image)
Single-site Pre-formed catalyst Nd-FC

Essence of the new catalyst development:

1. Single active catalytic species
2. Elimination of high molecular weight polymer species
3. Conversion of most Nd sites to active catalyst
4. High concentration catalyst: 0.28 mol Nd/l
5. Pre-form catalyst stable up to 6 months

Benefits:

a. Highly active catalyst: >99% conversion in 10 minutes, hence lower catalyst usage: improved cost effectiveness of Nd catalysis
b. Symmetrical narrow BR MW distribution, low PDI
c. Highest Nd-BR strength properties: higher Mn for a given Mooney
d. Lower solution viscosity: high MW rubber not present
e. Better processability of Nd-BR: faster uptake of Carbon Black
f. High CIS Content: >98%, low vinyl: 0.5%
g. Low rubber Gel content
h. Simple Mooney control through single component addition rate
Example of symmetrical MW distribution with single-site catalyst Nd-FC

Nd-FC catalyst activity

More than twice the concentration of active Nd catalyst centers
Same Nd/Al/Cl ratios, same Nd dosage
Comparison of MW Distributions

Latest generation Preform catalyst Nd-FC does not age
Product supplied in T-21 Isotanks

Registration

- EU Reach: in progress – by mid 2015
- USA: TSCA expected by end 2015