Improving ageing performance by the use of phenolic resin cure

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Acknowledgements

Resin cure team
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Dr Alexandra Krawicz (Resin R&D)
Paul-Pierre Piolé (Commercial lead)

China Lab Team
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Lui Yang
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The Substance Inside SI Group

- 2700+ Employees
- 1 Priority is Safety
- 90 Countries We Serve
- 20 Global Manufacturing Facilities
- 10 Market Segments
- 800+ Active Products
- $1+ Billion Annual Sales
- 1906 Year Founded
- Our Goal: 0 Negative Impact on Environment

SI Group, MPG 2018
<table>
<thead>
<tr>
<th>Our Market Segments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adhesives</td>
</tr>
<tr>
<td>Health &amp; Wellness</td>
</tr>
<tr>
<td>Additives</td>
</tr>
<tr>
<td>Chemical Intermediates</td>
</tr>
<tr>
<td>Engineering Plastics</td>
</tr>
<tr>
<td>Rubber</td>
</tr>
<tr>
<td>Fuels, Lubricants &amp; Oilfield</td>
</tr>
<tr>
<td>Surfactants</td>
</tr>
<tr>
<td>Industrial Resins</td>
</tr>
<tr>
<td>Specialty</td>
</tr>
</tbody>
</table>
SI Group Products For Rubber Applications

Reliability in plying-up processes:
• Tackifying resins

Increased hardness, modulus without high filler load:
• Reinforcing Resins

Lifetime adhesion without free resorcinol:
• Adhesion Promoting Resins

Superior heat ageing:
• Curing Resins
From Lab To Final Use
Raw Materials

(Very simplified)

Phenol

Formaldehyde

Alkene

Alkylphenol
Branched Novolac

Phenol / Formaldehyde Novolac
- Thermoplastic
- Non-linear
- Crosslinkable with a methylene donor
Linear Novolac

- Linear
- Thermoplastic

Alkylphenol Novolac
Linear Resol

Alkylphenol Resol
- Linear
- Thermoset
Resin Design

Depending on:
- The type of phenol (alkylated or not)
- The reaction conditions (ratio of phenol to formaldehyde, pH, temperature...)
- Addition of other monomers
- Post reaction of resin

The resin properties can be varied
- Thermoplastic or thermoset
- Molecular weight
- Linearity / branching
- Compatibility with rubbers
## SI Group Curing Resins

<table>
<thead>
<tr>
<th>Product Name</th>
<th>Cure Speed</th>
<th>Form</th>
<th>Methylol Content (%)</th>
<th>Melting Point (°C)</th>
<th>Benefits</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octyphenol Resol</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SP-1045</td>
<td>3</td>
<td>Flakes</td>
<td></td>
<td></td>
<td>An octyphenol resol based curing resin that offers moderate cure speed. Ideal for use in tire bladder manufacture to cure EPDM.</td>
</tr>
<tr>
<td>HRJ-10518</td>
<td>4</td>
<td>Flakes</td>
<td></td>
<td></td>
<td>An octyphenol resol curing resin that offers faster cure speed than other non-brominated alternatives.</td>
</tr>
<tr>
<td>Octyphenol Resol, Brominated</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SP-1055</td>
<td>7</td>
<td>Flakes</td>
<td></td>
<td></td>
<td>A brominated octyphenol based curing resin that offers very fast cure. With this product line, no need for added halogen donor. Ideal for small cross-section parts with short cure cycles.</td>
</tr>
<tr>
<td>Butylphenol Resol</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ELATOBOND® C650</td>
<td>3</td>
<td>Flakes</td>
<td></td>
<td></td>
<td>A PDPA free curing resin with moderate cure speed</td>
</tr>
<tr>
<td>ELATOBOND® C730</td>
<td>3</td>
<td>Flakes</td>
<td></td>
<td></td>
<td>A PDPA free curing resin with faster cure speed.</td>
</tr>
<tr>
<td>Special Alyphenol Resin in Oil</td>
<td></td>
<td>Liquid</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SMD-31214A</td>
<td>4</td>
<td>Liquid (30% solids content)</td>
<td></td>
<td>NA</td>
<td>Developed to cure EPDM for continuous production of TPV, this specialised resin is supplied in a compatible oil, ideal for use in liquid feed systems therefore easy to disperse.</td>
</tr>
</tbody>
</table>

*Indicative values from 1 (very slow) to 10 (extremely fast) in IR.

*If the solid resin, 3.4% if oil included.
Drivers For Better Ageing

Longer product life
• More tyre bladder cycles

Harsher usage conditions
• Higher underbonnet temperatures
• Higher component density

Market initiatives
• Cost of ownership / leasing models

So – Should we change the cure system?
Rubber Crosslinking Systems For Diene Rubbers
Crosslinking

The final rubber properties are a result of:
• Length of crosslinks
• Chemical nature of crosslinks
• Number of crosslinks

Aged / set behaviour depends on:
• Stability of rubber chains
• Stability of crosslinks
• Completeness of cure
**Alternative Vulcanisation Systems**

<table>
<thead>
<tr>
<th>Property</th>
<th>Sulphur</th>
<th>Peroxide</th>
<th>Traditional Resin Cure Cure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chain to chain bond type</td>
<td>C-S(_{(x)})-C</td>
<td>C-C(_{(x)})-C</td>
<td>C-C(_{(x)})-C</td>
</tr>
<tr>
<td>Curing speed</td>
<td>Slow to fast</td>
<td>Fast to very fast</td>
<td>Very slow to medium</td>
</tr>
<tr>
<td>Heat stability</td>
<td>Fair to good</td>
<td>Good to excellent</td>
<td>Good to excellent</td>
</tr>
<tr>
<td>Compression set</td>
<td>Fair to good</td>
<td>Good to excellent</td>
<td>Good to excellent</td>
</tr>
<tr>
<td>Cure method</td>
<td>Any</td>
<td>Not open air or open steam</td>
<td>Any</td>
</tr>
<tr>
<td>Advantages</td>
<td>Good ultimate mechanical and dynamic properties</td>
<td>High thermal stability, usable in either EPDM or EPM</td>
<td>High thermal stability, no free radicals</td>
</tr>
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</table>
Resin Cure Applications

Two major markets today
Tyre bladder (IIR)
• Repeated heat / stretch cycles

TPV (EPDM dispersed in PP)
• Good compression set
• Cured dynamically in twin-screw extruder
• No scission of polypropylene chain

What about other polymers?
Diene Rubbers

NR / IR
1 double bond every repeat unit

SBR
1 double bond every butadiene unit

NBR
1 double bond every butadiene unit, unless hydrogenated (HNBR)
Diene Rubbers

IIR
1 double bond every isoprene unit
Isoprene units a small % of total

EPDM (ENB type)
1 double bond every ENB unit
Double bonds not on main chain
ENB units a small % of total
What Does Resin Cure Need?

Suitable polymer
Resin
Metal halide – either added or made in situ
Generally acidic fillers
Resin Characteristics

Molecular weight and distribution
Methyolol content
Non-brominated or brominated
• brominated more active
Metal Halide

Acts as catalyst
Many effective metal halides impractical (hygroscopic)

Some practical halides

1. in-situ ZnCl$_2$, from reaction of chlorine containing polymer + ZnO
2. in-situ ZnBr$_2$, from brominated resin + ZnO
3. added SnCl$_2$:2H$_2$O
Other Ingredients

Generally need acidic conditions
- Clay better than CaCO$_3$
- Avoid CaO

Recent discovery – activated Zeolite as co-catalyst (Lanxess)
EP 2 441 798 A1 (Martin Van Duin, Philip Hough)
- Much quicker cure times
- Increased crosslink density
- Works with all metal halides tested
- Works with non-brominated and brominated resins
- Commercialised as stable masterbatch
# Effect Of Stannous Chloride And Zinc Oxide Level

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Description</th>
<th>Formulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Keltan 8550c (Arlanxeo)</td>
<td>EPDM, 5.5% ENB</td>
<td>100 100 100 100 100 100 100 100</td>
</tr>
<tr>
<td>Carbon black N550</td>
<td></td>
<td>70 70 70 70 70 70 70 70</td>
</tr>
<tr>
<td>Mistron Vapor (Imerys)</td>
<td>Talc</td>
<td>30 30 30 30 30 30 30 30</td>
</tr>
<tr>
<td>Paraffinic Oil</td>
<td></td>
<td>85 85 85 85 85 85 85 85</td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td>Rubber grade</td>
<td>2 2 2 2 2 2 2 2</td>
</tr>
<tr>
<td>Zeolite 70 (Rhein-Chemie)</td>
<td>68% zeolite in rubber</td>
<td>0 7.5 15 0 7.5 15 7.5 15</td>
</tr>
<tr>
<td>Stannous Chloride</td>
<td></td>
<td>1.5 1.5 1.5 0.8 0.8 0.8 0.4 0</td>
</tr>
<tr>
<td>SP-1045</td>
<td>Curing resin, 8-11% methylol</td>
<td>10 10 10 10 10 10 10 10</td>
</tr>
</tbody>
</table>

Mixing: 1 pass, lab internal mixer, end temperature target 95°C
RPA 145°C

MDR @ 145°C

- 10 zeolite, 1.5 SnCl₂
- 10 zeolite, 0.8 SnCl₂
- 5 zeolite, 1.5 SnCl₂
- 5 zeolite, 0.8 SnCl₂
- 0 zeolite, 1.5 SnCl₂
- 0 zeolite, 0.8 SnCl₂
- 5 zeolite, 0.4 SnCl₂
- 10 zeolite, 0 SnCl₂

Torque vs. Time (minutes)
Zeolite increasing MH, decreasing scorch and T90
SnCl2 has same effect but reaches a maximum
Optimisation possible for scorch / cure speed and MH by varying these ingredients
Work Remaining

This Study
• Physicals
• Ageing
• Extended cure test

Planned studies
• Vary resin type, resin level, ZnO level
• Other activation systems (brominated resin, halogenated polymers)
• Other polymers (IIR, HNBR)

Why?
• Provide advice on how to balance speed, processing, properties / aged properties in various polymers and applications
## Alternative Vulcanisation Systems

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Discussion / Conclusions

Industry needs are driving polymer and cure system choice

Resin cure can contribute to:
- Higher heat resistance
- Better ageing

Use of zeolite now means resin cure can be very fast
Discussion / Conclusions

Possible application areas:
Extrusions
Hoses
Conveyor belts
Drive belts

Need to consider:
• Processing and properties for each application
• Other components in the rubber part
Next Steps

Work on specific applications to confirm benefits
• Optimise formulations and processes
• Test to relevant standards
• Involve end users / specifiers
Questions?
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