Silane-Modified Polymers (SMP) – Combining the Best of Silicone & Organic Polymers

International Silicone Conference – May 17, 2016
Michael Austerberry, PhD – Wacker Chemical Corporation
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Agenda

- Introduction
  - Chemistry
  - GENIOSIL® SMP product line
- Formulating
- Manufacturing
- Performance in end-user products
What are Silane-Modified Polymer (SMP) Hybrids

SILICONES
- UV resistant
- high elasticity

POLYURETHANES
- paintable
- good mechanical properties

SMP HYBRIDS
- easy processing
- broad adhesion profile

ALPHA SMP HYBRIDS
- fast & reliable curing
- tin free formulations
- long shelf-life
Agenda

Introduction

Chemistry

GENIOSIL® SMP product line

Formulating

Manufacturing

Performance in end-user products
Chemistry of SMP Hybrid Polymers
1. modified silicones (MS)

Traditional “MODIFIED SILICONES”

- low viscosities
- good stability of the polymers
- broad adhesion profile

- low functionality
- very low reactivity, tackiness
- formulations very sensitive to moisture of fillers
- shelf-life limited
- limited mechanical properties
- tin catalyst needed
Chemistry of SMP Hybrid Polymers
2. silane-terminated polyurethanes (SPUR/STP-U) (method 1)
Chemistry of SMP Hybrid Polymers
2. silane-terminated polyurethanes (SPUR/STP-U) (method 2)

Traditional SILANE-TERMINATED POLYURETHANES (SPUR)

- good reactivity
- good crosslinking for improved elasticity
- broad adhesion profile
- higher strength

• very high viscosity (most polymers need plasticizers)
• sensitive to moisture of fillers
• critical towards crosslinking upon storage (faster skinning)
• limited possibilities in tin-free catalysis
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Low viscosity of silane-terminated polyethers

- easier handling in production
- better workability in formulations
- plasticizer free formulations
- high filler loading
- less scrapped material
- easier to gun
Chemistry of Hybrid Polymers
3. Silane-Terminated Polyethers (STP-E)

**SILANE-TERMINATED POLYETHERS (STP-E)**

Polymer OH + O=C=N \[\text{isocyanatoalkylalkoxysilanes}\] \[\text{urethane group}\]

<table>
<thead>
<tr>
<th>α</th>
<th>n = 1</th>
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<tbody>
<tr>
<td>Benefits α &amp; γ:</td>
<td></td>
</tr>
<tr>
<td>• 100 % functionality</td>
<td></td>
</tr>
<tr>
<td>• Tack-free curing</td>
<td></td>
</tr>
<tr>
<td>• Higher strength</td>
<td></td>
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<tr>
<td>• Low polymer content yet high performance</td>
<td></td>
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<tr>
<td>• Cost-efficient compounding</td>
<td></td>
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<tr>
<td>• Long shelf-life</td>
<td></td>
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</table>

<table>
<thead>
<tr>
<th>γ</th>
<th>n = 3</th>
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<tbody>
<tr>
<td>Additional benefits α:</td>
<td></td>
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<tr>
<td>• Very high reactivity &amp; fast strength-build-up</td>
<td></td>
</tr>
<tr>
<td>• Improved mechanical properties</td>
<td></td>
</tr>
<tr>
<td>• Crystal clear formulations</td>
<td></td>
</tr>
<tr>
<td>• Tin-free curing</td>
<td></td>
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</tbody>
</table>

| Additional benefits γ: |
| • Trimethoxy reaction → faster than MS |
| • Good recovery → sealants |
Rate of skin forming time of different endcapped SMP polymers

**α-STP-E**

**γ-STP-E**
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The GENIOSIL® “toolbox” of polymers provides many options

- **GENIOSIL® XT**
  - Polymer range for very strong and elastic adhesives and coatings

- **GENIOSIL® XB**
  - Polymer range for strong and hard adhesives and coatings

- **GENIOSIL® STP-E**
  - Standard polymer range for elastic adhesives & sealants

- **GENIOSIL® WP**
  - Polymer range for waterproofing liquid membranes

- **GENIOSIL® XM**
  - Polymer range for adhesion and elongation

- Most important of all – all polymers can be blended to achieve state-of-the-art products
Agenda

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GENIOSIL® SMP product line

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### Compounding with GENIOSIL® SMP’s

<table>
<thead>
<tr>
<th>Typical One-Component Formulation and Compounding Steps</th>
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<tbody>
<tr>
<td>10 - 40% silane-modified polymer</td>
</tr>
<tr>
<td>10 - 20% plasticizer</td>
</tr>
<tr>
<td>1 - 2% water scavenger</td>
</tr>
<tr>
<td>40 - 60% fillers, typically calcium carbonates</td>
</tr>
<tr>
<td>2 - 4% pyrogenic silica</td>
</tr>
<tr>
<td>1% stabilizer package</td>
</tr>
<tr>
<td>0.1 - 1% catalyst/adhesion = Aminosilane</td>
</tr>
</tbody>
</table>

- **pre-mix liquids**
- **disperse solids homogenously**
- **activate and evacuate bubbles**

**Compounding Steps:**
- screening recipe
- scale-up in lab
- transfer to production
Calcium carbonate selection impacts various properties

<table>
<thead>
<tr>
<th>Calcium Carbonate Type</th>
<th>Shear Strength</th>
<th>Rheology/Body</th>
<th>Elasticity</th>
</tr>
</thead>
<tbody>
<tr>
<td>GC</td>
<td>Low</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>GCC</td>
<td>Low</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>PCC</td>
<td>Low</td>
<td>High</td>
<td>High</td>
</tr>
</tbody>
</table>

GC = Ground Calcium Carbonate | GCC = Ground Coated Calcium Carbonate | PCC = Precipitated Coated Calcium Carbonate
Influence of formulation by plasticizers

- Shore hardness
- Viscosity
- Adhesion
- Through cure
- Skin formation time

![Graph showing elongation at break and viscosity changes with different plasticizers]
Pyrogenic Silica impact on mechanics

<table>
<thead>
<tr>
<th>HDK</th>
<th>Property</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET</td>
<td>Rheology/Body</td>
</tr>
<tr>
<td>QTY</td>
<td>Tensile Strength</td>
</tr>
<tr>
<td>BET</td>
<td>Elasticity</td>
</tr>
</tbody>
</table>
Stabilizer impact on product stability

<table>
<thead>
<tr>
<th>Stabilizer</th>
<th>Influence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antioxidant</td>
<td>Temperature</td>
</tr>
<tr>
<td>UV-Absorber</td>
<td>Radiation</td>
</tr>
<tr>
<td>HALS*</td>
<td>Temperature &amp; Radiation</td>
</tr>
</tbody>
</table>

* Hindered Amine Light Stabilizers
**α-Effect: fast without special catalysts**

Polymers cured with different catalytic systems

Skin-formation-time (23°C/50 % r.h.)

- **Benefits α-effect:**
  - no tin-catalyst required
  - easy formulation
  - improved storage stability
  - no degradation via secondary reactions with tin

GENIOSIL® GF 96 – Aminopropyltrimethoxysilane
DBTL – Dibutyltin-dilaurate
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Formulating approach with GENIOSIL® SMP

- Step 1: Charge mixing vessel
- Step 2: Mixing

Compounding Benefits at a Glance
- No heat activation in vessel
- No pre-drying of fillers
- No moisture monitoring during mixing
- No specific compounding parameters
- No special raw materials
- No hazardous ingredients

Fast and Easy Production Process

Total time is 1-2 hours before filling step
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SMP are capable of being formulated with performance from low modulus sealants to high performance adhesives.
GENIOSIL® SMP
The Bridge Between Silicones and Polyurethanes
Thank you for your attention!