Innovations in LSR Molding - New Materials & Technologies

Molding 2017, Charlotte NC, April 5th 2017

Oliver Franssen - Momentive Performance Materials GmbH, Leverkusen
Global Marketing - Elastomers Transportation

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Momentive Global Elastomer Production and R&D Sites

- Chino, CA
- Garett, IN
- Waterford, NY
- Lostock
- Leverkusen
- Shanghai
- Rayong
- Chennai
- Ohta
- Itatiba
- Bangalore
- Tech Service Centre (CC)
- R&D Centre

Polymers
- LSR/ LIM standard
- LSR/ LIM customed/ colored
- HCE base
- HCE customed

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In May of 1940, GE research chemist Eugene G. Rochow’s monumental discovery of the direct reaction process began the journey of scientific innovation that has led to the application of silicones in thousands of products that touch almost every aspect of daily life.
## Innovations & Market “Firsts”

### Industry Leadership through 75 Years of Silicone Innovation

<table>
<thead>
<tr>
<th>Year</th>
<th>Event</th>
</tr>
</thead>
<tbody>
<tr>
<td>1943</td>
<td>Peroxide vulcanization of silicone rubber</td>
</tr>
<tr>
<td>1940s</td>
<td>First “direct process” for making methylchlorosilanes</td>
</tr>
<tr>
<td>1950s</td>
<td>First non-hydrolyzable silicone surfactant for polyurethane foams</td>
</tr>
<tr>
<td>1962</td>
<td>First silane coupling agents for fiberglass and composites</td>
</tr>
<tr>
<td>1964</td>
<td>First construction sealant that hardens at room temperature</td>
</tr>
<tr>
<td>1969</td>
<td>First man walks on moon in silicone boot soles enabled by GE Silicones</td>
</tr>
<tr>
<td>1974</td>
<td>First true structural silicone glazing for architectural applications</td>
</tr>
<tr>
<td>1979</td>
<td>First commercialized silicone for 2-in-1 shampoo and conditioner</td>
</tr>
<tr>
<td>1986</td>
<td>First silicone polyethers introduced for textile treatment, laundry softeners and personal care</td>
</tr>
<tr>
<td>1996</td>
<td>First successful one-part addition cure technology for adhesives and pharmaceutical tubing</td>
</tr>
<tr>
<td>2001</td>
<td>First use of Silwet* hydrolytically stable super-spreader silicones for in-can pesticides</td>
</tr>
<tr>
<td>2004</td>
<td>First introduction of NXT* sulfur silane for next generation automobile tires</td>
</tr>
<tr>
<td>2008</td>
<td>First introduction of Next Generation Automotive Silicones</td>
</tr>
</tbody>
</table>

*NXT and Silwet are trademarks of Momentive Performance Materials Inc.*
LSR - Material and process overview
ASTM D2000 overview

Volume swell in IRM 903 oil [%]

Temperature [°C]

FFKM
FPM

VMQ = HCR / HV / HTV = LSR / LIM

FSL = FSE / FQE

FVMQ

EPDM
IIR
SBR
NR

not required

140
120
100
80
60
40
30
20
10

AEM, ACM, HNBR
CPE / CSM
CR
NBR, ECO

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LSR - overview

• Silopren* LSR is a 2-component, platinum catalyzed silicone elastomer with
  – Very low viscosity
  – Fast cure

• Supporting
  – Low injection pressure
  – Long flow path
  – Easy filling of complex cavities
  – Thin wall thickness

• Enabling
  – Multiple cavity moulds
  – High precision
  – Reproducable quality
  – Short cycle times
  – Fully automated injection processing (cold runner technology)
  – Flash-less processing, no secondary operations
  – Clean operation
  – Easy and flexible coloring of parts
  – Multicomponent molding eg. hard-soft combinations

Note: Test results. Actual results may vary.
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# Typical Physical Properties of Silopren* LSRs

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td></td>
<td>transparent to opaque</td>
</tr>
<tr>
<td>Viscosity (at RT, 10s⁻¹)</td>
<td>Pa s</td>
<td>10 – 900</td>
</tr>
<tr>
<td>Hardness</td>
<td>Shore A</td>
<td>5 – 90</td>
</tr>
</tbody>
</table>
| Tensile Strength                              | MPa psi   | 3 – 11
|                                               |           | 435-1600               |
| Elongation at Break                           | %         | 150 – 1000             |
| Tear Resistance                               | kN/m ppi  | 10 – 45
|                                               |           | 57-256                 |
| Density                                       | g/cm³     | 1,01 – 2,5             |
| Compression set (22 h - 175 °C / 350 F)       | %         | 15 - 35%               |

**General purpose**
- Self bonding
- Media resistant

**Food contact / FDA / USP**
- Oil bleeding
- Ultra-transparent

**Anti microbial**
- Fiber reinforced
- UV-curing

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Typical properties are average data and are not to be used as or to develop specifications. *Silopren is a trademark of Momentive Performance Materials Inc. Copyright © 2017 Momentive Performance Materials Inc. All rights reserved.
Addition Curing Principle

Polydimethyl-siloxan

\[
\begin{align*}
\text{Polydimethyl-siloxan} & \quad \text{Catalyst} \\
\text{Pt} & \\
\end{align*}
\]

Cross Linker

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Injection Molding Machine for Liquid Silicone Rubber

**Mold**
- Heated $\vartheta = 150 – 220 ^\circ C$
- Cold Runner; $\vartheta = 23 ^\circ C$
- Hardened steel for cavities
- Vacuum

**Injection Molding Machine**
- Standard Injection Molding Machine
- Special injection unit, $\vartheta = 23 ^\circ C$
- Optimized Non-Return Valve
- Control Pump and Handling

**Liquid Silicone Rubber**
- Viscous fluid
- 2 x 20 kg pail-kits or 2 x 200 kg drum kits
- Mixing ratio 1:1

**LSR Mixing/Metering Unit**
- Electric, pneumatic or hydraulic
- Material pressure ~ 200 bar
- Mixing ratio 1:1 additional color/additive line
- Static mixer and pressure reduction
Injection process – Cavity pressure

- filling without pressure
- injection time 0,5 - 5 sec
- holding pressure 0,1 - 2 sec
- under fill volumetric 95 - 98%

- increase of pressure through dilatation
- pressure in cavity 200 - 500 bar
- vulcanization 3 - 5 sec/mm
- demolding => shrink 2,5 - 4%
General mold-concept LSR

- Cavity plates
- Heating cartridges
- Insulation plates
- Chilled Moldframe

23 °C \( \theta \) = 150 – 220 °C 23 °C
Selfbonding LSR
New: Bonding to PC and copolyesters
2-Component Process-Technology Options

2-Component Molding

2 Shot Molding
- Index plate
- Rotating plate

Insert

Move between two IMM's
- individual cycles
- synchronic cycles

Self-Bonding

General Purpose

Drinking Water

Customized

Special Purpose

Silopren* LSR 2730 TP 3823
Silopren LSR 2740 TP 3783
Silopren LSR 2750 TP 3824
LIM* 9071 ET
Silopren LSR 2742
Silopren LSR 2752
CLS 8150
CLS 5000
Silopren LSR 2730
LIM 8040
CLS3060

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1. Preparation of combined test specimen by IM (Insert-Molding)

- Pellets of thermoplastic
- Injection molding of thermoplastic part
- Overmolding of LSR + additives possibly

2. Test of adhesion strength by peeling test

- Cohesive failure: strength of LSR < adhesion strength
- Adhesive failure: strength of LSR > adhesion strength

3. Peeling force [N/mm]

- 0: Separates with demolding
- 1-2: Stable Adhesion
- 3-6: Excellent Adhesion
- 7-10: Cohesive Failure

Note: Test results. Actual results may vary.

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New: Silopren* LSR 2739 (Self-Bonding LSR)

**Key Features and Typical Benefits**

- Self-bonding properties to thermoplastics including PC, PBT and copolyesters
- Lower temperature cure possible

**Potential Applications**

- Sealing elements, straps, respiratory masks or other hard-soft combinations

**Typical Physical Properties Silopren* LSR 2739**

<table>
<thead>
<tr>
<th>Property</th>
<th>Standard</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness</td>
<td>DIN 53 505</td>
<td>Shore A</td>
<td>32</td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>DIN 53 504 S2</td>
<td>N/mm²</td>
<td>8</td>
</tr>
<tr>
<td>Elongation</td>
<td>DIN 53 504 S2</td>
<td>%</td>
<td>650</td>
</tr>
<tr>
<td>Tear Resistance</td>
<td>ASTM D 624 die B</td>
<td>N/mm</td>
<td>30</td>
</tr>
</tbody>
</table>

1) Presscured slabs 10min/175 °C

**Engineering Thermoplastics**

<table>
<thead>
<tr>
<th>Thermoplastic</th>
<th>Suppliers</th>
<th>Peeling Force (N/mm) 24 h/RT</th>
<th>Peeling Force (N/mm) 4 h/100 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lexan® HP4 polycarbonate</td>
<td>Sabic Innovative Plastics</td>
<td>7,7</td>
<td>8,8</td>
</tr>
<tr>
<td>Apec® 1745 polycarbonate</td>
<td>Sabic Innovative Plastics</td>
<td>7,2</td>
<td>9,0</td>
</tr>
<tr>
<td>Lexan® HFD 1810 polycarbonate</td>
<td>Sabic Innovative Plastics</td>
<td>6,4</td>
<td>9,7</td>
</tr>
<tr>
<td>Lexan® 121 polycarbonate</td>
<td>Sabic Innovative Plastics</td>
<td>8,7</td>
<td>8,9</td>
</tr>
<tr>
<td>Makron® 2407 polycarbonate</td>
<td>Covestro AG</td>
<td>6,3</td>
<td>9,4</td>
</tr>
<tr>
<td>Makron® 2858 polycarbonate</td>
<td>Covestro AG</td>
<td>7,3</td>
<td>9,8</td>
</tr>
<tr>
<td>Makron® 2458 polycarbonate</td>
<td>Covestro AG</td>
<td>7,2</td>
<td>9,3</td>
</tr>
<tr>
<td>Panlure® L-1225Y polycarbonate</td>
<td>Teijin Limited</td>
<td>7,3</td>
<td>8,8</td>
</tr>
<tr>
<td>Tritan® TX1001 copolyester</td>
<td>Eastman Chemical Company</td>
<td>6,7</td>
<td>9,4</td>
</tr>
<tr>
<td>Tritan® TX 1501 HAT copolyester</td>
<td>Eastman Chemical Company</td>
<td>6,4</td>
<td>9,4</td>
</tr>
<tr>
<td>Ecozen® T120 copolyester</td>
<td>SK Chemicals</td>
<td>6,4</td>
<td>8,6</td>
</tr>
<tr>
<td>Ultradur® B4520 polybutylene</td>
<td>BASF AG</td>
<td>6,2</td>
<td>9,7</td>
</tr>
</tbody>
</table>

Note: Test data. Actual results may vary.
* Trademarks of their respective owners.
1 In accordance to DIN 53289.
Reduced Self Healing LSR
Key Features and Typical Benefits

- Reduce self-healing effect of slits, e.g. in valve applications
- Biocompatible, ISO 10993 and USP Class VI
- FDA and BfR compliant
- Sterilizable
- Available in 40 and 50 Shore A

Potential Applications

- Valves and fluid-flow products for food, medical and infant care

**Typical Physical Properties Silopren® LSR 2650 RSH ¹)**

<table>
<thead>
<tr>
<th>Property</th>
<th>Method</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>DIN 53 479 A</td>
<td>g/cm³</td>
<td>1.12</td>
</tr>
<tr>
<td>Hardness</td>
<td>DIN 53 505</td>
<td>Shore A</td>
<td>51</td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>DIN 53 504 S2</td>
<td>N/mm²</td>
<td>10</td>
</tr>
<tr>
<td>Elongation</td>
<td>DIN 53 504 S2</td>
<td>%</td>
<td>550</td>
</tr>
<tr>
<td>Tear Resistance</td>
<td>ASTM D 624 die B</td>
<td>N/mm</td>
<td>45</td>
</tr>
<tr>
<td>CS 22h/175 °C</td>
<td>DIN 53 517</td>
<td>%</td>
<td>25</td>
</tr>
</tbody>
</table>

¹) Presscured slabs 10 min/175 °C, postcured 4 h/200 °C
Slit Crack Simulation in Momentive Lab

Test sheet
- Injection molding of sheet (2 mm)
- Post curing (4 hours at 200°C)
- Apply defined slit (10 mm)
- Age after customer requirement

Preparation
- Fixed sheet on pressure chamber

Test
- Applied air pressure in water bath
- Recorded pressure when slit opens

Note: Test results. Actual results may vary.

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Self-Lubricating LSR
New: Medical Applications
Automotive Grades of Self-Lubricating Silopren* LSR

- **Self-Lubricating**
  - **Standard**
  - **Low Compression Set**
  - **Ultra Low Compression Set**
  - **Low Volatile**
New: Silopren* LSR 4655 SL

Key Features and Typical Benefits

- ISO10993 and USP Class VI compliant
- Automated assembly of devices and use activation enabled by lubricious surface
- Robust self-lubricating performance – longevity of molded articles

Potential Applications

- Needle-free access valves
- O-rings, stoppers and seals
- Other healthcare parts requiring assembly

### Typical Physical Properties Silopren LSR 4655 SL

<table>
<thead>
<tr>
<th>Property</th>
<th>Standard</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>DIN 53 479 A</td>
<td>g/cm³</td>
<td>1.13</td>
</tr>
<tr>
<td>Hardness</td>
<td>DIN 53 505</td>
<td>Shore A</td>
<td>55</td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>DIN 53 504 S2</td>
<td>N/mm²</td>
<td>8</td>
</tr>
<tr>
<td>Elongation</td>
<td>DIN 53 504 S2</td>
<td>%</td>
<td>450</td>
</tr>
<tr>
<td>Tear Resistance</td>
<td>ASTM D 624 die B</td>
<td>N/mm</td>
<td>45</td>
</tr>
<tr>
<td>CS 22h/175 °C</td>
<td>DIN 53 517</td>
<td>%</td>
<td>40</td>
</tr>
</tbody>
</table>

*1) Press cured slabs 10 min/175 °C

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Ultra Clear LSR
Innovative lighting applications need new materials. Ideal candidate should provide:

- High Transparency over a wide range of wavelengths
- Isotropic optical properties, no birefringence
- Low chromatic aberration
- Low thermo-optical coefficient
- High resistance to micro-cracking
- Temperature resistance from -40 °C up to > 150 °C
- High resistance against rapid climatic changes
- High resistance against ozone and strong UV-light
- Freedom of design
- High-precision molding of microstructured surfaces
- Highly efficient and automated injection molding process

**Objectives**

<table>
<thead>
<tr>
<th>Category</th>
<th>Property</th>
<th>LSR 7000</th>
<th>PC</th>
<th>PMMA</th>
<th>Glass</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Properties of Optical Clarity, 2 mm</strong></td>
<td>Transmission [%]</td>
<td>94</td>
<td>86–89</td>
<td>89–92</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>Index of Refraction (RI)</td>
<td>1.41</td>
<td>1.59</td>
<td>1.49</td>
<td>1.5–1.6</td>
</tr>
<tr>
<td></td>
<td>Haze %</td>
<td>&lt;1</td>
<td>1–3</td>
<td>2–4</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Abbe number</td>
<td>50</td>
<td>34</td>
<td>57</td>
<td>39–59</td>
</tr>
<tr>
<td></td>
<td>Yellowness index</td>
<td>&lt;1</td>
<td>1.0–3.0</td>
<td>1.0–3.0</td>
<td>-</td>
</tr>
<tr>
<td><strong>Durability</strong></td>
<td>Heat resistance</td>
<td>Excellent</td>
<td>Poor</td>
<td>Poor</td>
<td>Excellent</td>
</tr>
<tr>
<td></td>
<td>UV resistance</td>
<td>Excellent</td>
<td>Poor</td>
<td>Good</td>
<td>Excellent</td>
</tr>
<tr>
<td><strong>Design Freedom</strong></td>
<td>Complex/micro-design</td>
<td>Excellent</td>
<td>Good</td>
<td>Good</td>
<td>Poor</td>
</tr>
<tr>
<td></td>
<td>Material flexibility</td>
<td>Excellent</td>
<td>Poor</td>
<td>Poor</td>
<td>Poor</td>
</tr>
<tr>
<td></td>
<td>Light weight design</td>
<td>Excellent</td>
<td>Good</td>
<td>Good</td>
<td>Poor</td>
</tr>
</tbody>
</table>

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Examples of Existing Applications

Ultra-Transparent Silicone Elastomers

Pictures: Momentive Performance Materials, Kathod(1), Elmet(1)
UV Curing Silicones
UV Curing Silicones

Key Features and Typical Benefits

- On-demand, high-speed curing at low temperatures
- Biocompatibility – USP Class VI, ISO 10993 for most grades
- Combination with temperature-sensitive materials
- Encapsulation of electronic parts
- High precision
- Enables 3D printing of silicone elastomers

Typical Physical Properties

<table>
<thead>
<tr>
<th>Typical Physical Properties</th>
<th>Hardness [Shore A]</th>
<th>Density [g/cm³]</th>
<th>Tensile Strength [MPa]</th>
<th>Elongation at Break [%]</th>
<th>Tear [N/mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Addisil® UV Extrusion elastomer</strong> (1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Addisil UV 130 EX</td>
<td>29</td>
<td>1.08</td>
<td>12.0</td>
<td>660</td>
<td>20</td>
</tr>
<tr>
<td>Addisil UV 250 EX</td>
<td>50</td>
<td>1.16</td>
<td>12.1</td>
<td>920</td>
<td>45</td>
</tr>
<tr>
<td>Addisil UV 260 EX</td>
<td>60</td>
<td>1.17</td>
<td>10.5</td>
<td>580</td>
<td>47</td>
</tr>
<tr>
<td>Addisil UV 270 EX</td>
<td>66</td>
<td>1.20</td>
<td>9.6</td>
<td>420</td>
<td>29</td>
</tr>
</tbody>
</table>

| **Silopren® UV Curing General Purpose LSR** (2) |                   |                 |                        |                         |            |
| Silopren UV LSR 2030        | 28                | 1.10            | 8.0                    | 750                     | 20         |
| Silopren UV LSR 2060        | 59                | 1.15            | 13.0                   | 500                     | 25         |

| **Silopren UV Curing Electro LSR** (2) - Tracking Resistance 3.5 kV |                   |                 |                        |                         |            |
| Silopren UV Electro 225-1   | 25                | 1.07            | 4.5                    | 580                     | 9          |
| Silopren UV Electro 235-2   | 35                | 1.09            | 4.6                    | 520                     | 15         |

(1) Two part Addisil elastomer, mixing ratio 100:0.5
(2) UV cured LSR with a mixing ratio 100:2

Laboratory Vulcanization Conditions: exposure to a Hg-(Fe-doped) middle pressure lamp for 2 min at 80 mW/cm² intensity, without further heat curing.
Sample Application: Soap holder made during K 2013

- Injected and mold PP article
- Inserted PP in cavity for UV LSR
- Injected UV LSR in steel cavity
- Illuminated and cured UV LSR through PP
Material Data for
Sigmasoft Virtual Molding
**Few Typical Physical Properties at RT – not helpful for Simulation**

**Typical Physical Properties**

<table>
<thead>
<tr>
<th>Property</th>
<th>Comp. A</th>
<th>Comp. B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>Translucent</td>
<td>Translucent</td>
</tr>
<tr>
<td>Viscosity in Pa·s $\eta_R = 10$ s$^{-1}$ at 20°C</td>
<td>DIN 53018</td>
<td>550</td>
</tr>
<tr>
<td>The pot-life of the mixture of the two components (closed vessel) at 20°C is usually three days. Increased temperatures reduce the pot-life.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td>DIN 53 479 A</td>
<td>g/cm$^3$</td>
</tr>
<tr>
<td>Hardness</td>
<td>DIN 53 505</td>
<td>Shore A</td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>DIN 53 504 S2</td>
<td>N/mm$^2$</td>
</tr>
<tr>
<td>Elongation at Break</td>
<td>DIN 53 504 S2</td>
<td>%</td>
</tr>
<tr>
<td>Tear Strength</td>
<td>ASTM D 624 die B</td>
<td>N/mm</td>
</tr>
<tr>
<td>Compression Set 22 h at 175°C</td>
<td>ISO 815</td>
<td>%</td>
</tr>
</tbody>
</table>


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Curing at different temperatures
Measured on Monsanto MDR

Crosslinking = f (temperature)

Note: Test results. Actual results may vary.
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# Material Properties Silopren* LSR 2670

Viscosity = f (temperature and shear rate)

Measured on cone / plate

<table>
<thead>
<tr>
<th>Viscosity [Pas]</th>
<th>23 °C</th>
<th>50°C</th>
<th>70°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSR Component</td>
<td>0,9 s⁻¹</td>
<td>5 s⁻¹</td>
<td>10 s⁻¹</td>
</tr>
<tr>
<td>2670</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>1190</td>
<td>740</td>
<td>500</td>
</tr>
<tr>
<td>B</td>
<td>1500</td>
<td>760</td>
<td>525</td>
</tr>
</tbody>
</table>

Note: Test results. Actual results may vary.

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### Data Silopren* LSR 2670

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal conductivity</td>
<td>0.22 W/mK</td>
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<tr>
<td>Heat Capacity $c_p$</td>
<td>1.23 J/gK</td>
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<tr>
<td>Thermal expansion coefficient</td>
<td>$2.4 \times 10^{-4}$ 1/K</td>
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<tr>
<td>Poisson’s Ratio</td>
<td>0.5</td>
</tr>
</tbody>
</table>

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Silopren® LSRs material laws / current snapshot

<table>
<thead>
<tr>
<th>Materials</th>
<th>Group Filter</th>
<th>Short Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silopren_7070FC</td>
<td>All</td>
<td>LSR, hardness 39 Shore A, scorch as 2% curing degree, no-flow 10% curing degree,</td>
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<tr>
<td>Silopren_7080HP</td>
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<td>MOMENTIVE</td>
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<tr>
<td>Silopren_LSR-2070</td>
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<tr>
<td>Silopren_LSR-2630</td>
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<td>Silopren_LSR-2550</td>
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<td>Silopren_LSR-2560_ZKS</td>
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<td>Silopren_LSR_7580-40</td>
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</table>

Typical properties are average data and are not to be used as or to develop specifications.

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†Sigmasoft is a trademark of SIGMA.
Examples, Simulation vs. Reality at Momentive

CVA „Ursula“ Bottlenet - Fakuma 2015

- Shotweight 70 gr
- Flowlength 620mm
- Asymmetric gate
- Match between simulation and reality

Elmet „Eggcup“ – K 2016

- Silicone on Silicone bond
- 4+4 cavity
- Shotweight 61 gr
- Incl. simulation of pneumatic piston pump

Pictures from Sigma Engineering (2), CVA Silicone (1), Momentive Performance Materials (7)
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