An example of thermoset – Silicone

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Silicones 101

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Overview

• From Sand to Silicone
• Silicone Terminology and Silicone Building Blocks
• Unique Properties of Silicones
• Building Silicone Polymers
• Healthcare Applications
Silicon in the Earth

Composition of the Earth's Crust:
- Oxygen: 46.6%
- **Silicon**: 27.7%
- Aluminum: 8.1%
- Iron: 5.0%

Overall Composition of the Earth:
- Iron–56: 34.6%
- Oxygen–16: 29.5%
- **Silicon–28**: 15.2%
- Magnesium–24: 12.7%
- Nickel–56: 2.4%
- Sulfur–32: 1.9%
1. **Chlorosilane synthesis**: Si + 2 MeCl → SiMe₂Cl₂
2. **Chlorosilane hydrolysis**: SiMe₂Cl₂ → “SiMe₂(OH)₂” → HO(SiMe₂O)ₙH + (SiMe₂O)ₙ
3. **Polymerization**: Me₃SiOSiMe₃ + (SiMe₂O)ₙ → Me₃SiO(SiMe₂O)ₙSiMe₃
# Terminology and Terms

<table>
<thead>
<tr>
<th>Terminology</th>
<th>Definition</th>
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<tbody>
<tr>
<td>Sil icon</td>
<td>The silicon atom or silicon metal</td>
</tr>
<tr>
<td>Sil ane</td>
<td>Typically small molecules with one or more Si atoms</td>
</tr>
<tr>
<td>Sil oxane</td>
<td>Typically a polymer with Si-O-Si repeating backbone</td>
</tr>
<tr>
<td>Sil anol</td>
<td>Any Si-OH functionality</td>
</tr>
<tr>
<td>Silicone</td>
<td>Generic term for Si based materials</td>
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</tbody>
</table>
Siloxane Internal (Core) Structure / Nomenclature

Endcap

Monofunctional
Organic
Soft & Flexible
Linear

Me₃SiO₁/₂

Linear/Cyclic

Difunctional

Me₂SiO₂/₂

Networking

Trifunctional

MeSiO₃/₂

Tetrafunctional
Inorganic
Hard & Brittle
Rigid Network

SiO₄/₂

* Q is derived from “quadrifunctional” to distinguish it from T for trifunctional
Polydimethylsiloxanes (PDMS)

- Silicones have a backbone which is inorganic, like glass
- The side groups are organic: typically methyl
- The degree of polymerization varies from $n=0$ up to several thousand
- Silicones show low viscosity, even at very long chain lengths

<table>
<thead>
<tr>
<th>$n$</th>
<th>Viscosity (cst)</th>
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</thead>
<tbody>
<tr>
<td>64</td>
<td>100</td>
</tr>
<tr>
<td>320</td>
<td>1,000</td>
</tr>
<tr>
<td>730</td>
<td>10,000</td>
</tr>
<tr>
<td>1300</td>
<td>50,000</td>
</tr>
</tbody>
</table>

Chain has spiral shape

PDMS Polymers: Range of viscosities available: 0.65 cst - 1,000,000 cst
Characteristics of Si-O bond and Methyl Substitution in Polydimethylsiloxane (PDMS)

- High Bond Angle
  - C-C-C ~ 109 degree
  - C-O-C ~ 111 degree
  - Si-O-Si ~ 130 degree
  WIDER

- Large Bond Length
  - C-C ~ 1.54 Å
  - C-O ~ 1.43 Å
  - Si-O ~ 1.64 Å
  LONGER

- High Bond Energy of Si-O
  - C-C ~ 83 kcal/mole
  - C-O ~ 86 kcal/mole
  - Si-O ~ 106 kcal/mole
  STRONGER
Fundamental Characteristics Provide Unique Capabilities

1. Low intermolecular forces between methyl groups
   - Low surface tension: $21.6 \gamma_L \text{ mN/m (PDMS fluid)}$
   - Low glass transition temp (Tg at $-123^\circ \text{ C}$)

2. Wide O-Si-O bond and low rotational energy = very flexible chain
   - Rotational energy: $E(\text{Si-O}) = 3.3 \text{kJ/mole}$ vs. $E(\text{C-C}) = 13.8 \text{kJ/mole}$
   - Presence of high free volume (high permeability)

3. High bond energy of the siloxane bond leads to higher thermal stability
   - C-C $\sim 83 \text{ kcal/mole} \rightarrow$ C-O $\sim 86 \text{ kcal/mole} \rightarrow$ Si-O $\sim 106 \text{ kcal/mole}$

4. The partial ionic nature of the siloxane bond
   - Si-O bond has a 41% ionic character
Silicones Can Be Modified…
to target desired properties

• Adds reactivity to the polymer (crosslinking, other)
• Increases/decreases thermal stability
  — Longer alkyl chain decreases thermal stability
  — Phenyl groups increase thermal stability
• Affects siloxane chain flexibility
  — Generally, bulkier groups reduce chain flexibility which affects $T_g$, surface tension, and viscosity index
• Can modify the hydrophile-lipophile balance
  — Provide a broad range of surfactant properties
• Increases compatibility with hydrocarbon systems
• Modifies chemical resistance
Building Around PDMS Polymers

Product forms:
- Pure polymers
- Blends
- Emulsions / Dispersions
- Elastomer / Rubber

Organic Functionality
- Alkyl
- Polyether
- Amino
- Dimethyl
- Phenyl

Molecular Structure
- Linear
- Cyclo
- Cross Linked
- Resinous

Molecular weight
- Volatile Fluid
- Non-Volatile Fluid
- Viscous Fluid
- Gum
Changing Molecular Structure

Ring Polymer (Cyclomethicone)

Linear Polymer (Dimethicone)

Crosslinked Polymer (Gel, Rubber)

Resin
Why Silicones Excel in Healthcare Applications?

**Silicone Elastomers/Tubing**
- Purity
- Bio-compatible
- Easy to sterilize
- Long proven history in market

**Silicone Adhesives**
- Long-term adhesion
- Promote easy and comfortable removal
- No skin irritation or sensitisation

**Silicone Excipients**
- Increase compatibility;
- Optimize effectiveness
- Improve aesthetics – non-greasy, silky feel
- Improve spreading

**Versatile and Biocompatible**
- Various physical forms – liquid to solid, hard to soft, …
Lubrication with Silicones

The physico-chemical properties of PDMS are closely related to their usage in siliconization.

Numerous parenteral components are "siliconized"

- **Glass & Plastic (syringes, vials, cartridges)**
  - Limit contact wear (glass to glass) and dust generation
  - Ensure efficient draining / emptying and reduce dosage errors
  - Reduce break loose and reduce gliding force (syringes)

- **Rubber (piston, stoppers)**
  - Ensure smooth handling during manufacture, use

- **Metal (needles)**
  - Improve flow (laminar)
  - Reduce pain
Dimethicone Emulsions (Silicone-in-Water)

- Silicones don’t mix with water
- Water and dimethicone are immiscible
- However, water is often the preferred solvent for dilution and coating
  - Emulsion technology makes this possible
  - Silicone “oil” can be combined with water using surfactants
Silicone Antifoams – Simethicone Compounds

• Role of the silicone fluid
  – Insoluble in water
  – Low surface and interfacial tension
  – Hydrophobe the silica
  – Facilitate bridging and rupture of the foam walls

• Role of the silica
  – Facilitates entry at air/water interfaces

Foam is a dispersion of gas in liquid stabilized by adsorbed surfactant film.

Fluid droplets which collide with the interface will more frequently deform or flatten rather than penetrate and break the film...

For dewetting to occur, the particle must penetrate the surfactant film.
Silicone Elastomers: A Typical Formulation

- A functional polydimethylsiloxane (PDMS) polymer
  - LSR (fluid based) or HCR (gum based)

- Reinforcing filler, perhaps an extending filler
  - An unfilled system has a tensile strength of approximately 50 psi versus ~1000 psi for a filled one
  - Extending fillers do not “tie-in” to the polymer matrix and as such, weaken the material to some degree
  - Extending fillers are used to impart some type of “unique” property to the cured material

- Process Aides
  - Small chain fluids to treat the surface of the silica

- Cure Package
Cure Packages

• Components of the reaction that cause our elastomers to cure or vulcanize. Reaction needs a catalyst or initiator to occur at an appreciable rate.

Typical Catalysts are:
- Platinum: Catalyst in one of a two part system
- Peroxides*: Used only in HCRs

* Technically considered an initiator as it is consumed in the reaction.
Platinum Cure Chemistry

Disadvantages:
- Cure easily inhibited by sulfur, amines, phosphates and some metals
- Two components
- Not easy to produce

Advantages:
- Good deep section cure
- No by-products
- Catalyst used in low concentration
- Little shrink
Peroxide Cure Chemistry (free radical)

- Peroxides are effective at levels around 1%
- By-product remain after cure that is not intrinsic part of the cured article and can be a potential extractable
Liquid Silicone Rubber vs. High Consistency Silicone Rubber

- LSRs contain “Fluid” base polymers, HCRs contain “Gum” base polymers
- The silica filler in LSRs is “treated” or pacified much better than in HCRs
- Cross-link density, per a given durometer, is higher in LSRs
- HCRs have much better green strength making them the best option for extrusion applications
Basic Elastomer Technology
High Consistency vs. Low Consistency Processing

**HCR**
- Mill softening and catalyzation
- Preform
- Vulcanization
- Finishing

**LSR**
- Meter-mix
- Process [mold, extrude film]
- Finishing
## Summary of Unique Properties of Silicones

<table>
<thead>
<tr>
<th>Molecular Characteristics</th>
<th>Physico-Chemical Properties</th>
<th>Applications</th>
</tr>
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<tbody>
<tr>
<td>❖ Siloxane backbone:</td>
<td>❖ Low surface tension &amp; energy</td>
<td>❖ Lubricant</td>
</tr>
<tr>
<td>• Open</td>
<td>❖ High spreading and wetting capabilities</td>
<td>❖ Antifoaming</td>
</tr>
<tr>
<td>• Flexible</td>
<td>❖ Permeable to gas and water vapor</td>
<td>❖ Release agent</td>
</tr>
<tr>
<td>• Mobile</td>
<td>❖ Heat stability</td>
<td>❖ Aesthetic feel (softness)</td>
</tr>
<tr>
<td>❖ High bond strength</td>
<td>❖ Low degradability</td>
<td>❖ High temperature processing</td>
</tr>
<tr>
<td>• 435 kJmol⁻¹ Si-O</td>
<td>❖ Compatibility with organics</td>
<td>❖ Can be sterilized</td>
</tr>
<tr>
<td>• cf. 350 kJmol⁻¹ C-C</td>
<td>❖ Weather resistance</td>
<td>❖ Emulsions</td>
</tr>
</tbody>
</table>

*Silicones are characterized by their unique properties, which are advantageous in various applications.*
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