Silicones in Food Contact Materials

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Food Packaging Forum

Food Packaging Forum (FPF)

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Dossier – Silicones

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1 Introduction

Silicones form a highly versatile class of polymers that are, e.g. in the form of fluids, rubbers or resins, commonly used as food contact materials (FCMs). Silicones are generally water-repellent thermostable, non-reactive and highly gas permeable. Although some of their further properties, e.g. flexibility and versatility, are also common in plastic, the underlying chemistry of these polymer classes differs fundamentally. Silicones have a backbone of silicon (Si) and oxygen and two organic groups are generally bound to the silicon atoms. In contrast, the backbone of plastic mainly consists of carbon atoms. Silicones do not occur in nature and the silicon-carbon bonds are very persistent to biological degradation.

2 Definitions and nomenclature

The terms "siloxanes" and "silicones" are often used as synonyms describing molecules with an oxygen-silicon backbone (-Si-O-Si-O-Si-O-Si). Each Si atom of such a backbone usually carries two organic groups such as methyl, ethyl or phenyl (R). For the description of oligomeric species the terms "siloxane" or "siloxane oligomer" are generally used, whereby polymers are mostly designated as "silicones" or "polysiloxanes". The Si-O backbones can be linked together by chemical reactions leading to a huge variety of silicones. Different structural elements of siloxanes are sometimes notified by the symbols M, D, T and Q, which are based on the number of Si-O bonds per structural unit (Table 1). Siloxanes composed of difunctional D-units are linear, whereas the tri- and tetrafunctional T- and Q-units lead to cross-linking of the polymer (**1**, Figure 1). Monofunctional M-units are present at the terminal ends of the siloxane molecules. This nomenclature facilitates the simple designation of siloxane oligomers, as exemplified for

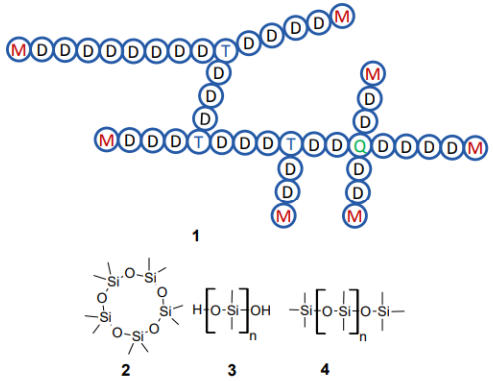


Figure 1. (**1**) Schematic illustration of a cross-linked silicone resin (refer to Table 1). Chemical structures of (**2**) the cyclic siloxane D_5 and (**3**) hydroxyterminated polydimethylsiloxane (PDMS) and (**4**) methylterminated PDMS (MD_nM).

3 Physical and chemical properties

A huge variety of siloxane-based compounds is available. These products cover a broad range of properties and are applied for many different purposes. However, silicones share certain characteristics. The most common and simple silicone is unmodified and non-copolymerized polydimethylsiloxane (PDMS; **3**, Figure 1). PDMS is highly flexible and has a low boiling point and low viscosity that is only slightly influenced by temperature. PDMS can behave like a

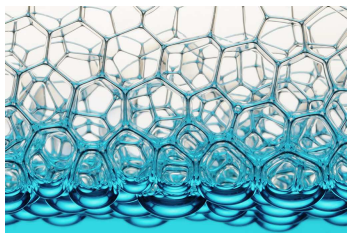
Source: https://www.foodpackagingforum.org/fpf-2016/wp-content/uploads/2015/11/FPF_Dossier09_Silicones.pdf

Examples: Silicones in contact with food

Kitchen utensils:	baking molds, spoons, ice cube trays, bags, stoppers, for bottles, gaskets, sealings,…
Food industry:	lubricating oils, release agents, conveyor belts, coatings, tubing, valves, O-rings,…
Food packaging:	additives in plastics and paper & board packaging, coatings of natural corks,…
Babies & toddlers:	baby soothers, feeding teats,…
Food additives:	food-grade antifoaming agents, protective layer on fats and oils, additive in cooking spray,…







Claims

Reusable alternative Eco-friendly
Long-lasting Ocean friendly Less wasteful

Comprised mainly of inert silica (sand) and oxygen.

Recyclable?
Call your local recycling center.

Endures for decades unchanged & resists degradation of sun and sea.

?

Won't degrade into microfragments in our oceans.

Exceeds EU and USA food safety standards.

Questions

We need to understand

- the chemical properties and areas of applications
- migration and exposure data
- human and environmental hazards
- knowledge gaps

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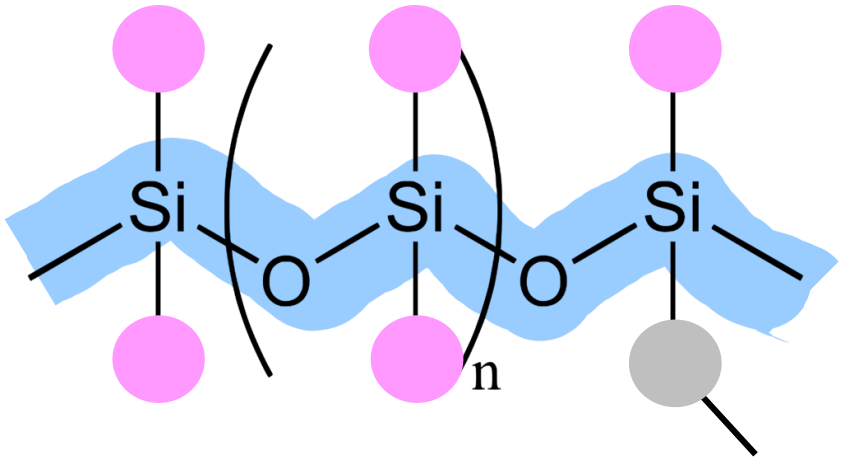
Chemistry of silicones (= polysiloxanes)

Polymers with an inorganic oxygen-silicon backbone and organic side groups.



Backbones can be linked via side groups.

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Common properties of silicones

- High thermal stability
- Low chemical reactivity
- Water & oil repellent
- High gas permeability
- Insoluble in water, mineral oil, alcohol
- Uptake of hydrophobic molecules possible
- Susceptible to hydrolysis by acids or bases

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US regulation

Silicones are regulated as indirect food additives by the US FDA under C.F.R., Title 21 on Food and Drugs, parts 170 to 199

178.3570 (lubricants with incidental food contact)
177.2600 (rubber articles intended for repeated use)
177.2465 (polymethylmethacrylate / poly-(trimethoxysilylpropyl)methacrylate copolymers)
175.300 (resins and polymer coatings)
175.320 (resins and polymer coatings for polyolefin films)
177.1200 (cellophane)
175.105 (adhesives)

Prior sanctioned ingredients and substances generally recognized as safe (GRAS) are also allowed in the production of silicones.

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European regulation

Framework Regulation (EC) 1935/2004, Article 3

> Materials and articles [. . .] shall be manufactured [. . .] so that, under normal or foreseeable conditions of use, they do not transfer their constituents to food in quantities which could endanger human health.

No harmonized regulation in the EU on silicones.

Germany: BfR Recommendation XV

France: Arrêté du 25 Novembre 1992

Council of Europe: Resolution on the use of silicones in food contact applications

Annex I of the EU Plastics Regulation (EU) 10/2011 lists six polysiloxanes

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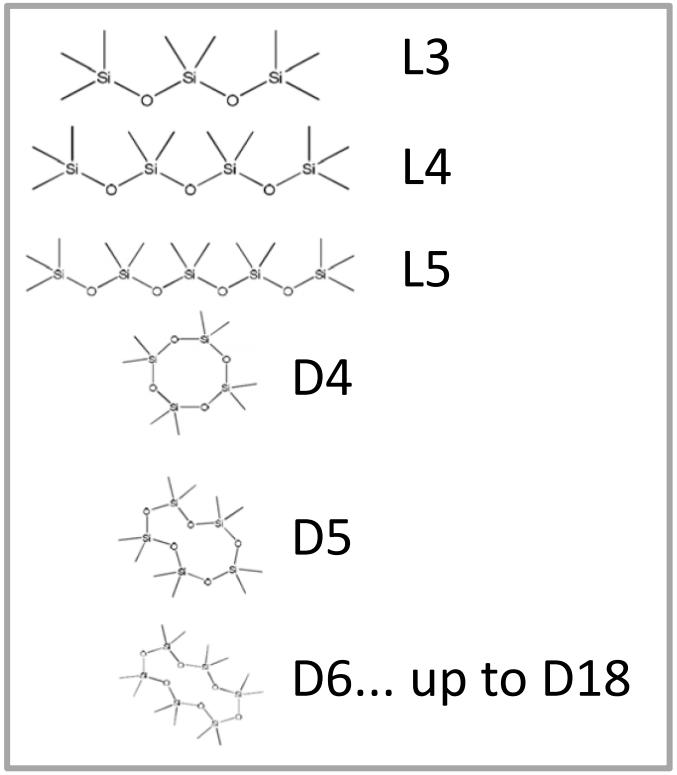
Types of migrants

- Siloxane oligomers
- Additives
- Catalysts
- Breakdown and reaction products



The smaller, the more volatile!

General observations

- Most studies address the migration siloxane oligomers: cyclic oligomers (D) migrate at higher levels than linear oligomers (L).
- Volatile cyclic oligomers measured in the air during/after baking in silicone molds.[a]
- Silicone molds emit higher levels of particles into indoor air than metal molds.[a]
- Levels of migration usually decrease after repeated cycles.
- Extraction may exceed proposed action limits, whereas migration tests stay below.[b]
- Silicone baking molds can loose substantial amounts of their mass during use at high temperatures (>0.5%).
- Fat molecules migrate from the food into the molds and may cause hygienic problems.
- Only few studies address the migration of “non-silicone” substances.

Sources: FPF Dossier (2015) Silicones, doi:105281.zenodo/33522;
[a]Fromme H et al. (2019) Environment International, 126: 145-52;
[b]Cederberg TL & Jensen LK (2017) National Food Institute, DTU

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Example:
“non-silicone” migrants from silicone baby bottles

- Test conditions: 5 silicone baby bottles
  food simulant (50% ethanol)
  2 hours, 70°C
- 31 substances identified and quantified, for example: phthalates, DIPN, benzophenone, naphthalene, aldehydes
- “This material generally showed migration of a greater number and extent of substances than [polypropylene]”

Source: Simoneau C et al. (2012) Food Additives & Contaminants A; 29:469-80

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Exposure to chemicals from silicones in contact with food

Cyclic silicone oligomers:

- Further sources, e.g. cosmetics
- Additional routes: inhalation, ingestion, dermal absorption
- Volatile substances rather quickly eliminated via breathing
- D4, D5, D6 currently included in *Biomonitoring California*

“Non-silicone“ migrants:

- More data needed!

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Cyclic siloxane oligomers

High-dose animal toxicity studies

- Impaired fertility, (reversible) histopathological changes, changes in hormone levels, no genotoxicity, immunomodulatory activity

Current risk assessment & management under REACH

- D4, D5, D6 are Substances of Very High Concern (persistent, bioaccumulative, toxic); on the Candidate List for authorization
- D4, D5: Use in wash-off cosmetic products restricted under Annex XVII of REACH

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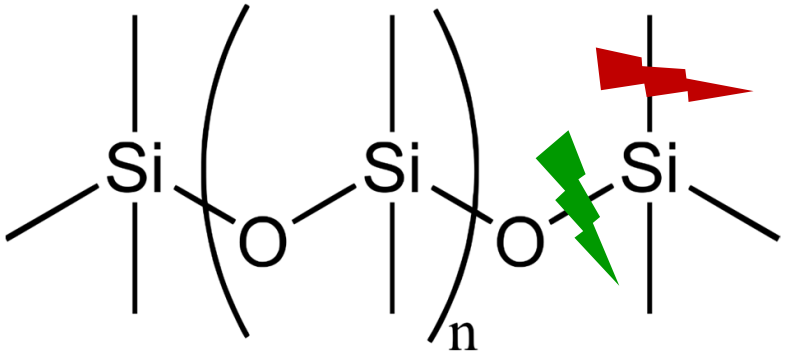
Environment



Degradation:

- Si-O bonds are rather easily (bio)degradable
- Si-C bonds are not degradable by known microorganisms
- Fate of incomplete degradation products unknown

Recycling:

- technology based on chemical recycling
- no collection schemes for consumers

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Conclusions

- Silicones are materials with unique properties that can be used for various applications.
- Furthermore, silicones are often strongly promoted as safe and environmentally friendly alternative to plastic.
- However, we should carefully evaluate whether the use of silicones in contact with food may be of concern for human health or the environment.
- Therefore, we need to better understand the properties of known migrants, identify unknown migrants and consider the fate of silicones at their end-of-life.

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Save the date!

FPF workshop – 24 October 2019, Zurich

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