Food
Packaging
Forum

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 decamethylcyclopentasiloxane that is accordingly named D_5 (**2**, Figure 1).

Linear oligomers and polymers have the chemical formula $[R_2SiO]_n$. Such oligomers are notified by the abbreviation L followed by the number of units (e.g. octamethyltrisiloxane is named L_3). The structure of the most common silicone, polydimethylsiloxane, is illustrated in Figure 1 (**3** and **4**). Cross-linked siloxanes can be described by the general formula $[R_nSiO_{(4-n)/2}]_m$ with n being between 1 and 3, $m \geq 2$ and R being an organic group.

Table 1. Structural elements of silicones.

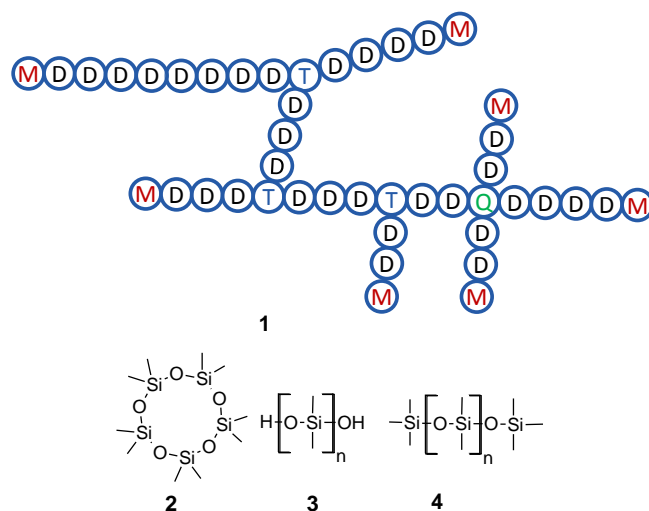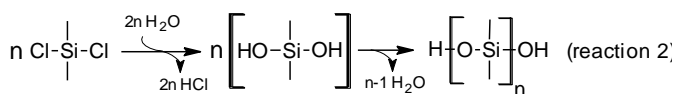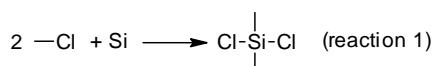| Structural units	Functionality	Simplified notation
R–Si–O– (R, R)	Monofunctional	**M**
R–Si–O– (R, O)	Difunctional	**D**
R–Si–O– (O, O)	Trifunctional	**T**
–O–Si–O– (O, O)	Tetrafunctional	**Q**

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 viscous liquid or an elastic solid. Materials composed of PDMS have a low surface tension. In general, silicones are water and oil repellent. They are insoluble in water, mineral oil and alcohols and have a good chemical and thermal stability. In aqueous environment, they bind to organic-rich matter, e.g. sediment. Silicones easily take up small molecules of similar hydrophobicity and contact with oils or solvents may change the material properties of silicones. The Si-O bonds of silicones are susceptible to hydrolysis by acids or bases and especially do not withstand strong mineral acids, e.g. hydrochloric and sulfuric acid [1, 2]. In 2014, the physiochemical properties of cyclic siloxane oligomers, including water solubility, vapor pressure, partitioning coefficients and bioaccumulation potential, were summarized by Wang et al. [3].

4 Chemical synthesis

The first step in the synthesis of PDMS, the most common silicone, is usually the reaction of elemental silicon with methyl chloride (reaction 1). This process results in a chlorosilane mixture in which dichlorodimethylsilane is the most abundant product. Dichlorodi-methylsilane easily hydrolyzes to the corresponding alcohol (silanol), which carries two OH-groups and is unstable under reaction conditions. In the presence of the hydrochloric acid produced, the silanols easily undergo self-condensation yielding linear or cyclic polymers (reaction 2). Branched polymers can be produced by the addition of trichloromethylsilane (CH_3SiCl_3) or tetrachlorosilane ($SiCl_4$).

$$2\ \text{—Cl} + \text{Si} \longrightarrow \text{Cl-Si-Cl} \quad \text{(reaction 1)}$$

$$n\ \text{Cl-Si-Cl} \xrightarrow[\text{2n HCl}]{\text{2n H}_2\text{O}} n\left[\text{HO-Si-OH}\right] \xrightarrow{\text{n-1 H}_2\text{O}} \text{H}\left[\text{O-Si}\right]_n\text{OH} \quad \text{(reaction 2)}$$

5 Types of silicones

Structural formulae and information about the application of a wide variety of commercially available silicones and silicone starting substances is often provided by manufacturers (e.g. [4]).

5.1 Silicone fluids, gums and greases

Silicone fluids are generally based on PDMS and contain linear and cyclic oligomers and polymers. In such a mix, linear PDMS molecules are either terminated by trimethylsiloxy (M) or silanol units. The molecular weight (MW) of silicone fluids usually ranges between 4000 and 25'000. In case polymers with MW >100'000 are produced, their viscosity is increased and they are alternatively named silicone gums. Silicone greases used for lubrication are prepared by dispersing silica fillers and soaps, e.g. lithium stearate, into the formulation.

5.2 Silicone rubbers

Liquid silicones can be cross-linked by different methods to produce silicone rubbers (=elastomers). Silicone rubbers are typically reinforced with fumed silica or mixed with different minerals, e.g. calcium carbonate or metal oxides to reduce the production costs.

High temperature vulcanization (HTV)

HTV silicone rubbers are most commonly produced on the basis of silicone gums with a typical MW of 300'000–700'000, which are cross-linked (=vulcanized) by the addition of strong peroxides. Peroxides approved for food contact and used for the vulcanization of silicones under heat include bis(2,4-dichlorobenzoyl) peroxide, dibenzoyl peroxide and dicumyl peroxide. These processes often produce volatile siloxane oligomers and peroxide by-products, which are generally removed in a post-curing process by incubation at high temperatures.

Room temperature vulcanization (RTV)

Alternatively, silicone rubbers can be synthesized by vulcanization at room temperature. For this purpose silanol-terminated polymers of intermediate MW are incubated in the presence of suitable reagents (e.g. tetrafunctional silicate esters) and catalysts (e.g. tin- or platinum-based). Since the cross-linking reaction already starts at moderate temperatures, the two components are usually kept separately and labelled with the acronym RTV-2. Alternatively, the cross-linking reaction of silicone rubbers can be initiated by atmospheric moisture, which allows providing one-component systems (RTV-1).

5.3 Silicone resins

The main differences between silicone resins and RTV rubbers are the mechanisms and the degree of cross-linking. Silicones that are used for the production of resins contain not only di-, but also tri- and tetrafunctional siloxane units in the polymer backbone (T and Q units, Table 1, Figure 1), which provide OH-groups in the backbone as branching points for cross-linking. Stable solutions of silicone are prepared by removing all water. They can then be stored until the cross-linking is initiated by heat or the addition of catalysts such as zinc octanoate [5].

5.4 Silicone copolymers

Most of the available silicone polymers are composed of dimethylsiloxane units, but copolymers including vinyl- or phenylsiloxane groups are also used commercially. Methylphenyl-siloxanes have a lower service temperature than PDMS and improved heat resistance. For FCMs the formation of certain cyclic phenylsubstituted PDMS shall be prevented by choosing suitable starting materials [6]. Silicone copolymers are often applied in the form of silicone resins. Silicones with fluoroalkyl groups have an improved resistance to solvent, fuels and oils while being stable at a wide range of temperatures, but they are not reported to be used in food contact.

5.5 Silicone as additives in polymers

Silicones are added to thermoplastic polymers including polyolefins, polystyrene and acrylonitrile-butadiene-styrene to enhance the flow during manufacture [1]. Low percentage levels of silicone enhance the surface finish of thermoplastics. Furthermore, they are used in the manufacture of polyurethane foams.

6 Applications
6.1 Industrial applications

In food packaging and processing plants silicone fluids are broadly used as release agents on a wide variety of materials and equipment. Silicone lubricating oils are used in bearings and gears with rolling friction to maintain the functioning of machines [7]. Permanent or temporary silicone coatings prevent sticking of food or food packaging to different surfaces, e.g. conveyor belts, ovens, freezing trays, and baking tins. Tubing, conveyor belts, O-rings, stoppers, valves and milk liners in direct contact with food are often made of silicones rubbers.

6.2 Household uses

Silicone products find wide application as kitchen utensils. In households they are frequently used as baking molds, spoons, coasters, spatula, dough scrapers, brushes, containers, ice cube trays, stoppers for bottles and many more. These kitchen utensils

Figure 2. Examples of silicone-containing FCMs.
Photos: courtesy of Nerissa's ring, Piulet, Didriks, Greg and Sam Howzit, www.flickr.com.

are exclusively made out of silicone or they are combined with other materials such as metal or different kinds of plastic. Gaskets for e.g. pressure cookers and electric kettles are often made of silicone rubber. Silicones are used as adhesive sealants in e.g. refrigerators, catering equipment and sinks. Silicone-polyester resins are found as coatings in thermally stressed appliances such as toasters, cookers and pans.

6.3 Food packaging

Silicones are used as additives in plastics to improve processing, molding, fire resistance and surface properties. Silicones are used in the pulp and paper industry to prevent foaming, as additives in the finishing process of paper and tissues and for de-inking during paper recycling [7]. Silicones are further applied as plastic release liners in clear film labels on beverage bottles and other food containers [7]. Natural corks for alcoholic beverage bottles are often coated with silicones [8].

6.4 Products for babies and toddlers

Silicone rubbers are widely used to produce baby soothers, feeding teats and nipple shields for breast-feeding.

6.5 Silicones as food additives

Silicones are used in many types of FCMs and as processing aids during food production and processing (e.g. as anti-foaming agents during crop treatment, sugar production, fermentation, washing of vegetables and potatoes, and processing of beverages) [7]. Furthermore, they are used as a protective layer on fats and oils to prevent them from oxidation. Since PDMS is widely used in FCMs and also listed in the food additives legislation (E900) it fulfills the criteria of "dual-use additives" according to the Union Guidelines on Regulation (EU) No 10/2011 [9].

7   Market data

Several comprehensive market studies on silicones were recently issued, but they are not freely available [10-12]. The information summarized in this dossier was obtained from press releases and published digests of these market studies that refer to only limited data. Silicones are used in many sectors such as energy, electrical and electronics, building and construction, automotive and transportation, pharmaceutical and healthcare, chemicals, aviation and aerospace, and others. Although they are also widely used in food contact, no specific data on this sector were presented, but may be found in the full versions of the market studies.

- In 2013, about US $15.5 billion were globally earned with silicone compounds [10]. A report forecasts the U.S. demand for silicones to be US $4.3 billion in 2018 [12].
- In the U.S. and Western Europe, silicone fluids and rubbers were identified as the two leading product types, which together account for more than 85% of the market value in 2013 [10, 12].
- The market research institute Ceresana forecasts the global silicone market to grow annually by 5.0% until 2021 [10] and growth rates of 3.2% p.a. were estimated for the U.S. until 2018 [12]. Another market study predicts compound annual growth rates of 7.6% over the period 2014-2019 [11].
- China is the largest consumer of silicones worldwide, followed by Western Europe and the U.S. [10]. In 2013, Asia-Pacific accounted for more than 50% of the worldwide silicone output.
- According to two market studies the following companies are key players in the global silicone market: Bluestar Silicones, Dow Corning Corp., Momentive Specialty Chemicals Inc., Shin-

Etsu Chemical Co. Ltd., Evonik, China National Blustar and Wacker Chemie AG [10, 11].
- Further production figures were summarized in a recent review article on siloxanes [2]. Based on these numbers the annual production of silicones was assumed to be several million tons.

8   Current regulations
8.1 European Union

In Europe, no harmonized legislation exists for silicone materials used as FCMs. Under the Framework Regulation (EC) 1935/2004 silicones are included on the list of FCM articles and materials for which specific measures shall be established [13]. In 2004, the Council of Europe, which is an independent body and not controlled by the EU, published a resolution on the use of silicones in food contact applications [6]. In the resolution the types of silicones and product groups are defined and the general topics migration, manufacture and labelling are addressed. An overall migration limit of 10 mg/m^2 surface area, or alternatively 60 mg/kg food, is recommended. These two values are identical to the overall migration limits defined in the Plastics Regulation (EU) No 10/2011. The formation of certain cyclic phenylsubstituted PDMS shall be prevented by the appropriate choice of starting materials. The resolution is accompanied with the Technical Document No. 1, which includes inventory lists of approved and non-approved chemicals to be used in the manufacture of silicones for food contact applications. In Germany and France, the use of silicones is regulated on a national level by the Recommendation XV from the BfR [14] and by Arrêté du 25 Novembre 1992 [15], respectively. In Europe, further national regulations exist that cover the use of silicones as FCMs [1]. The Commission Directive 93/11/EEC defines specific migration limits for N-nitrosamines and N-nitrosatable substances released from elastomers or rubber teats and soothers [16].

A database search for "siloxanes" revealed six polysiloxanes currently listed on Annex I of Commission Regulation (EU) No 10/2011 to be used in plastic FCMs. One specific PDMS (CAS 156065-00-8) is authorized as co-monomer in the production of polycarbonate, the other five PDMS-based substances may be used as additives in plastic FCMs. The lists of substances for non-plastic FCMs, which were compiled by the EFSA Scientific Cooperation (ESCO) Working Group in 2011 [17], contains different silicones to be used either directly or in the manufacture of paper and board, coatings and rubbers. These compounds are partially subject to national regulations by EU Member States and the details can be found in Annex I of the ESCO list.

8.2 United States

Silicones used in FCMs are generally regulated as indirect food additives by the U.S. Food and Drug Administration (FDA) under C.F.R., Title 21 on Food and Drugs, parts 170 to 199 [18]. Silicones are covered in many sections of this regulation, e.g. under section numbers 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) and 175.105 (adhesives). A database providing yearly updates can be accessed and searched on the website of the FDA. In the production of silicones, prior sanctioned ingredients and substances generally recognized as safe (GRAS) are also legally allowed.

9 Migration

Substances that may migrate from silicone-based materials into food include additives, catalysts, oligomers, breakdown and reaction products [1]. Cyclic and linear silicone oligomers and low MW siloxanes are potential migrants of all silicone product groups. HTV and RTV silicone rubbers and silicone resins may also contain residual levels of catalysts that potentially migrate into food. Examples include peroxide curatives and their break-down products, and platinum, zinc or tin catalysts. A possible oxidation product and migrant of silicone rubbers and resins is formaldehyde. Migration from silicones can occur directly into the food, but volatile organic compounds (VOCs), e.g. many siloxane oligomers, may also partition into the gas phase. Migration of VOCs has to be especially considered when the silicone product is intended to be used at elevated temperatures (e.g. baking trays).

Silicone FCMs may be tested by a so-called compositional fingerprint determination of the material. This fingerprinting allows the analysis of molecules in silicone products having the potential to migrate into food. Migration studies using the intended food or food simulants may then be performed based on the results of the fingerprinting (Figure 3, [1]). Methods for the trace analysis of siloxane oligomers in different matrices were reviewed by Rücker and Kümmerer including the levels of detection and quantification [2]. Several examples of migration studies from silicone FCMs are listed and summarized below.

- In 2012, Zhang and colleagues investigated the migration of three cyclic (D_4, D_5 and D_6) and three linear siloxane oligomers (L_3, L_4 and L_5) from food-grade silicone fluids, silicone nipples and kitchen utensils into milk, infant formula and liquid simulants [19]. Extraction experiments showed that the product samples contained cyclic and linear siloxanes at levels between a few mg per kg up to a few g per kg. In all tested samples the amount of the linear siloxanes extracted from the nipples was below the detection limit. A cake pan displaying high siloxane concentration was chosen for further migration tests. No migration was observed into milk and infant formula, but concentrations of the cyclic siloxane D_6 reached 155 ng/ml

when 95% ethanol was used as simulant for fatty food.

- Between 2009 and 2012, a set of detailed studies comprising the migration from silicones into food and food simulants was published by Helling and colleagues [20-22]. The group of scientists investigated silicone baking molds and teats under actual conditions of use, analyzed the migration of siloxane oligomers, volatile organic compounds and platinum, and quantified the uptake of fat and proteins. In 2009, they validated a ^{1}H-NMR method to measure overall migration from silicone baking molds [21]. The migration from silicone baking molds strongly depended on the food or food simulants used. The migration into simulants for fatty foods reached levels of 35-40 mg/dm^2 after the first cycle of use and strongly decreased with each subsequent cycle. However, the migration into the cake was lower (1.0-1.2 mg/dm^2), but remained almost stable over 10 cycles. In 2010, it was concluded that the freely available fat level has a major impact on the migration of siloxane oligomers [20]. The researchers illustrated this by preparing different foods in silicone molds. Siloxane concentrations of more than 1000 mg/kg food were measured in the fat separating from meat loafs, exceeding the overall migration limit of 60 mg/kg food manifold. The concentrations in the meat itself were ~30-fold lower than in the separated fat. In all baking experiments, reverse migration of fat from the food into the silicone was observed. The levels of fat typically reached 0.5%, which may lead to questions regarding hygienic issues. In 2012, the team of scientists focused on the long-term use of polysiloxanes [22]. The migration of siloxane oligomers from pizza molds was in the range of 0.9-1.2 mg/dm^2 for the first 10 baking cycles and steadily decreased over the next 1700 cycles. The migrating siloxane oligomers were almost completely replaced by triglycerides originating from the food. Nevertheless, the physical properties remained stable over the life-time of the molds.

- In 2005, a Rapra review report was published detailing the results of a Foods Standards Agency (FSA) project (A03046): The migration of low MW compounds from ten commercial silicone products was investigated by using a range of

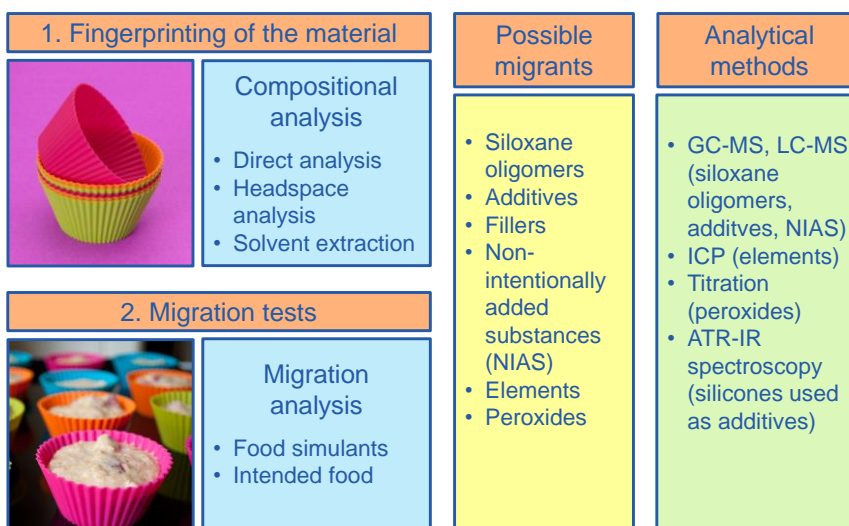| 1. Fingerprinting of the material	Possible migrants	Analytical methods
Compositional analysis • Direct analysis • Headspace analysis • Solvent extraction	• Siloxane oligomers • Additives • Fillers • Non-intentionally added substances (NIAS) • Elements • Peroxides	• GC-MS, LC-MS (siloxane oligomers, additves, NIAS) • ICP (elements) • Titration (peroxides) • ATR-IR spectroscopy (silicones used as additives)
2. Migration tests **Migration analysis** • Food simulants • Intended food		

Figure 3. Safety assessment of silicone-based FCMs by analyzing the material's composition and by migration testing. The different groups of possible migrants (e.g. oligomers, additives, peroxides) may be identified and quantified by a variety of chromatographic and spectroscopic methods, e.g. gas or liquid chromatography coupled with mass spectrometry (GC-MS, LC-MS), inductively coupled plasma scans (ICP) or attenuated total reflectance infrared spectroscopy (ATR-IR).
Photos: courtesy of Didriks and Йоана Петрова, www.flickr.com.

analytical techniques. Overall migration from silicone rubbers was higher than from silicone resins, which is caused by the highly cross-linked matrix of the resins. The total amounts of siloxane oligomers migrating from silicone rubbers and resins were mainly based on the presence of the cyclic molecules D_4-D_8. Migration of cyclic siloxanes from silicone rubbers reached 0.05 and 0.56 mg/dm^2 in water and olive oil, respectively. The concentrations of siloxane oligomers migrating from silicone resins stayed below the detection limit for most food simulants, but 13.2 µg/dm^2 of oligomers were detected when olive oil was used.

- In the same year, the Swiss Federal Office of Public Health investigated the heat stability of baking molds and came to the conclusion that the tested products were stable at temperatures up to 150°C, but 70% of the tested molds lost more than 0.5% of their weight after 4 hours at 200°C [23]. Although the weight loss was much lower after further heating cycles, the products were judged to be non-compliant with some national legal requirements [14, 15].
- Silicone baby bottles were part of an analytical migration study performed by the European Commission Joint Research Centre (JRC) in 2012 [24]. 31 different substances were identified and quantified in the migrate of silicone baby bottles. Amongst others, the bottles leached substances related to printing inks, e.g. benzophenone and diisopropyl naphthalene, several phthalates, e.g. diisobutyl phthalate, diethylhexyl phthalate and dibutylphthalate, and aldehydes.
- A Dutch retail survey investigated the migration of N-nitrosamines, N-nitrosatable substances and 2-mercaptobenzthiazol (MBT) from baby bottle teats and soothers [25]. These chemicals may be introduced during the vulcanization process. None of the tested products based on silicone rubbers exceeded the migration limits for potentially carcinogenic N-nitrosamines and N-nitrosatable substances as it is defined in the Commission Directive 93/11/EEC, and MBT was not detected at all.
- In 2012, Elskens and colleagues developed a predictive algorithm for assessing the global migration from silicone molds [26]. Since silicone molds are usually intended to come into repeated contact with foodstuffs, three replicates are recommended for compliance testing. Based on data of two replicate migration experiments the algorithm shall help to predict the expected level of migration for the third replicate. Thus the compliance of the material may be judged while saving the time and analytical costs for the third migration experiment.
- In 2007, different siloxane oligomers such as D_4, D_5, D_6 and L_5 were analyzed from the volatile mix of chemicals released from the packaging after cooking microwave popcorn [27].

10 Toxicology and risk assessment

The migration studies described above have shown that FCMs made of silicones may leach a variety of different chemicals into the food. This section mainly focusses on the toxicological properties of siloxane oligomers, which are the most typical and largest group of migrants [1]. They are commonly found as reaction by-products in many silicones used in contact with food.

10.1 Linear siloxane oligomers

In 2013, hexamethyldisiloxane (L_2, CAS 107-46-0) was added to the Community Rolling Action Plan (CoRAP) of the European Chemicals Agency (ECHA) based on its proposed carcinogenic, mutagenic and reprotoxic properties [28]. In March 2015, three further linear

siloxane oligomers (octamethyltrisiloxane (L_3, MDM, CAS 107-51-7), decamethyltetrasiloxane (L_4, MD$_2$M, CAS 141-62-8) and dodeca-methylpentasiloxane (L_5, MD$_3$M, CAS 141-63-9)) were listed on CoRAP due to their potential bioaccumulative, persistent and toxic properties [29]. The evaluation, which is scheduled for the period 2015-2017, shall clarify if the manufacture and/or use of these substances may pose a risk to the environment or to human health. Environment Canada evaluated the potential risk of MDM to the environment and human health in a screening assessment, which also included data on three structural linear analogues hexamethyldisiloxane, MD$_2$M and MD$_3$M [30]. According to the report, only limited empirical health effect data was available, but MDM and its analogues affected the liver, kidney and lung, and decreased the body weight gain in rats following repeated-dose exposure.

10.2 Cyclic siloxane oligomers

In 2007, several peer-reviewed studies on reproductive toxicity and endocrine disrupting effects of the cyclic siloxane octamethylcyclo-tetrasiloxane (D_4, CAS 556-67-2) and decamethylcyclopentasiloxane (D_5, CAS 541-02-6) were published by researches from Dow Corning [31-35]. Rats were exposed to up to 700 and 160 ppm of D_4 and D_5, respectively, by whole-body vapor inhalation. For each compound, a two-generation study was performed [32, 33] and the effects of multiple and single day exposure regimes on only female rats were analyzed additionally [31]. In animal experiments, D_4 caused impaired fertility by affecting the female rat's reproductive cycle and by reducing the pregnancy rate, number of pups born and litter size [31]. D_4 exhibited low affinity for the estrogen receptor-α *in vitro*. This result was supported by further *in vivo* studies in which D_4 caused a weak estrogenic response [35, 36]. For D_5 no reproductive toxicity has been concluded from two inhalation [33, 35] and one oral study [36]. A 2-year toxicity study resulted in a statistically significant increase of uterine tumors in rats when they were exposed to vapors of 160 ppm of D_5 [37]. Another target organ that was affected by D_4 and D_5 was the liver [3]. Oral and inhalation studies with D_4 and D_5 led to increased liver weight in the test animals. The lung, adrenal, thymus and kidney were also reported to be affected by oral or inhalation exposure to D_4 and D_5 [3, 38, 39].

Several regulatory authorities assessed the risks of D_4, D_5 and/or D_6. D_4 and D_5 were both judged to be very persistent and very bioaccumulative (vPvB) by the ECHA PBT expert group, while D_4 is also persistent, bioaccumulative and toxic (PBT) [40]. D_4 is suspected of damaging fertility (CLP regulation: hazard statement code H361f). D_4 is on the Danish list of PBT and vPvB substances and it shall be phased out in Sweden [3]. In 2008, Environment and Health Canada published three screening assessments for D_4, D_5 and D_6 and concluded that D_4 and D_5 may have an immediate or long-term harmful effect on the environment or its biological diversity, but not on human health [38, 39, 41]. In 2011, the conclusion for D_5 was revised based on the general judgement that "D_5 does not pose a danger to the environment" [42]. The British Environment Agency concluded in 2009 that "no risks are identified to the air, water, and the terrestrial compartments, nor to humans exposed via the environment from the production and all uses of D_5" [43].

11 Exposure

Besides FCMs antifoaming agents that are based on silicones and added directly to food are another food-related exposure source of siloxane oligomers. These compounds are also present in a wide variety of goods used in daily life such as personal care and consumer products. Siloxane oligomers may be released from all these different sources during processing, storage, service life and

disposal. Thus, total exposure estimation has to consider the different sources and exposure routes (e.g. ingestion, inhalation, dermal absorption). Several studies report on the exposure to cyclic and linear siloxanes from personal care products and indoor air, but oral exposure estimates for these compounds are scarce and mainly based on the few available migration studies.

- Daily exposure to cyclic and linear siloxane oligomers from personal-care products was estimated to be 307 mg for adult women in the U.S. [44]. This amount refers to the siloxane oligomers that come into contact with the skin or may be inhaled after evaporation, but it does not indicate the actual uptake.
- In 2015, the inhalation exposure to linear and cyclic siloxane oligomers was assessed by Tran and Kannan based on measurements from the vapor and particular phase of indoor air from Albany, New York, U.S [45]. The authors estimated an average total inhalation siloxane exposure dose of 19 μg/person/day. In 2014, similar studies from other countries, e.g. China, Italy, and the UK, were reviewed, in which daily exposure levels ranging from ng to mg were measured [2].
- Occupational exposure to cyclic and linear siloxanes was measured in blood plasma of workers from a silicone recycling factory in China [46]. The average concentrations of methyl siloxanes were 5.61-451 and 4.56-13.5 ng/g blood plasma for workers and the control group, respectively. The elevated concentrations in the workers were positively correlated with the exposure levels during the siloxane production processes.
- According to Rücker and Kümmerer no data regarding the incorporation of volatile siloxanes in food are available. However, the authors judge inhalation followed by skin absorption to be the most prevalent exposure pathways [2].
- In 2007, Siddiqui and colleagues stated that there is essentially no oral exposure to D_5 [33].

12 Environmental issues

12.1 Occurrence in the environment

Cyclic and linear siloxane oligomers have been measured in air, surface waters, sediment, process effluents and waste waters, soil, sludge from waste water treatment plants and biota. In 2014, data on the almost ubiquitous occurrence of cyclic and linear siloxanes in aqueous systems, biota, non-aqueous liquids, soil and dust, air and biogas were summarized [2]. In 2012, Wang et al. also reviewed the sources and occurrence of cyclic siloxane oligomers in the environment [3]. The measured levels and types of siloxane oligomers strongly varied between the studies, but few general conclusions were drawn by the authors. In influents of sewage treatment plants, sludge and sediments the concentrations of cyclic siloxanes were generally higher than linear oligomers. Siloxanes were found in organisms living in remote areas and could have been subject to long-range transport after emission from human settlements. In air, siloxane concentrations increase from rural over suburban to urban sites. D_4 and D_5 were the two most abundant siloxanes in outdoor and indoor air. Fairly high concentrations of D_4 and D_5 reaching several milligrams per m^3 were measured in biogas derived from landfills and sewage treatment plants. Concentrations of these compounds in indoor air were lower than in biogas and higher than in outdoor air.

12.2 Degradation

In soil, silicones such as linear PDMS can be degraded by hydrolysis to volatile compounds of lower MW. Under suitable conditions these degradation products, typically silanols, may again condensate and form other siloxanes or they alternatively evaporate. Clay minerals can act as catalysts and enhance the degradation of silicones in soil. Alkaline reaction conditions strongly increase the degradation rates. Several hydrolytic enzymes, e.g. esterases and lipases, catalyze the degradation of Si-O bonds. Conversion of cyclic siloxane oligomers to linear silanols was also observed in mammals [47] and microorganisms were reported to convert silicones by hydrolytic reactions [48].

In contrast to the easily breakable Si-O bond, the Si-C bond is much more difficult to cleave. However, this reaction can occur by OH-radicals attacking the methyl C-H bond in the atmosphere and it was also observed in higher organisms including mammals. In 2014, Rücker and Kümmerer summarized the evidence for biotic cleavage of Si-C bonds by microorganisms and concluded that no experimental observations as yet justified the conclusion of siloxanes being biodegradable on a practically useful scale. According to the authors, no complete mineralization, including the cleavage of all Si-C bonds, was ever observed. If confirmed this would imply that molecules with Si-C bonds were persistent in the environment.

Knowledge gaps exist regarding the degradation of cross-linked silicone rubbers and resins, because the properties of one of their main degradation intermediates, methylsilanetriol $MeSi(OH)_3$, are almost unknown [2].

12.3 Recycling

Although silicones are valuable and expensive polymers, silicone recycling is in its infancy. Recycling processes are based on depolymerization [49, 50], since mechanical recycling is generally not feasible due to the high temperature stability of silicones. Industrial waste that is only composed of silicone is more easily recyclable than consumer waste, in which the silicone is often bound to other materials or used as a coating on surfaces.

Glossary

Silanes are a class of chemical compounds with the general formula Si_nH_{2n+2}. In structural silane analogues the hydrogen atoms can be replaced by halogens, alky or alkoxy groups, sulfhydroxy or hydroxyl groups, amine, epoxides or by combinations thereof.

Silanol is a functional group in silicon chemistry with the connectivity Si-OH. They are e.g. as terminal group in PDMS.

Silicone and *siloxane* are often used as synonyms describing molecules with an oxygen-silicon backbone (-Si-O-Si-O-Si-O-Si). For the description of oligomeric species the terms "*siloxane*" or "*siloxane oligomer*" are generally preferred, whereby polymers are mostly designated as "*silicones*" or "*polysiloxanes*".

Abbreviations

ATR-IR	Attenuated Total Reflectance Infrared Spectroscopy
D_4	Octamethylcyclotetrasiloxane
D_5	Decamethylcyclopentasiloxane
D_6	Dodecamethylcyclohexasiloxane
CAS	Chemical Abstracts Service
CoRAP	Community Rolling Action Plan
ECHA	European Chemicals Agency
EFSA	European Food Safety Authority
ESCO WG	EFSA Scientific Cooperation Working Group
FCM	Food Contact Material
FDA	U.S. Food and Drug Administration
FSA	Foods Standards Agency
GC-MS	Gas Chromatography-Mass Spectrometry
GRAS	Generally Recognized As Safe
HTV	High Temperature Vulcanization
ICP	Inductively Coupled Plasma Scan
JRC	European Commission Joint Research Centre
LC-MS	Liquid Chromatography-Mass Spectrometry
MBT	2-Mercaptobenzthiazol
MDM	Octamethyltrisiloxane
MW	Molecular Weight
NIAS	Non-Intentionally Added Substances
PBT	Persistent, Bioaccumulative and Toxic
PDMS	Polydimethylsiloxane
RTV	Room Temperature Vulcanization
SML	Specific Migration Limit
vPvB	Very Persistent and Very Bioaccumulative
VOC	Volatile Organic Compound

References

1. Forrest MJ. 2005. Silicone products for food contact applications. Rapra Review Reports 188. 16:124.
2. Rücker C, and Kümmerer K. 2015. Environmental chemistry of organosiloxanes. Chem Rev. 115:466-524.
3. Wang D-G, Norwood W, Alaee M, et al. 2013. Review of recent advances in research on the toxicity, detection, occurrence and fate of cyclic volatile methyl siloxanes in the environment. Chemosphere. 93:711-25.
4. Nanjing SiSiB Silicones Co., LTD. 2014. SiSiB Silicones. [http://www.powerchemcorp.com/library/public/SiSiB_SILANES_SILICONES_8c_print.pdf]
5. Wicks ZW, Jones FJ, Pappas SP, et al. 2007. Organic Coatings: Science and Technology, Third Edition, John Wiley & Sons, Inc., Hoboken, NJ, USA.
6. Council of Europe, Committee of Ministers. 2004. Resolution ReSAP(2004)5 on silicones used for food contact applications.
7. Andriot M, Chao SH, Colas A, et al. 2007. Industrial applications of silicones. In: Inorganic Polymers. R. De Jaeger and M. Gleria, eds., Nova Science Publishers. pp 61-161.
8. Ortega-Fernández C, González-Adrados JR, García-Vallejo MC, et al. 2006. Characterization of surface treatments of cork stoppers by FTIR-ATR. J Agric Food Chem. 54:4932-6.
9. European Commission. 2014. Union Guidelines on Regulation (EU) No 10/2011 on plastic materials and articles intended to come into contact with food.
10. Ceresana. 2014. Market Study: Silicones (UC-7905). [http://www.ceresana.com/en/market-studies/plastics/silicones/]
11. ReportsnReports. 2015. Global silicones market 2015-2019. [http://www.reportsnreports.com/reports/335356-global-silicones-market-2015-2019.html]
12. Freedonia. 2014. Silicones - US industry study with forecasts for 2018 & 2013. [http://www.freedoniagroup.com/brochure/31xx/3138smwe.pdf]
13. Regulation (EC) No 1935/2004 of the European Parliament and of the Council of 27 October 2004 on materials and articles intended to come into contact with food and repealing Directives 80/590/EEC and 89/109/EEC.
14. Bundesinstitut für Risikobewertung. 2014. XV. Silicone.
15. Ministère de l'économie et des finances. 1992. Arrêté du 25 novembre 1992 relatif aux matériaux et objets en élastomères de silicone mis ou destinés à être mis au contact des denrées, produits et boissons alimentaires.
16. Commission directive 93/11/EEC of 15 March 1993 concerning the release of the N-nitrosamines and N-nitrosatable substances from elastomer or rubber teats and soothers.
17. EFSA. 2012. Report of ESCO WG on non-plastic Food Contact Materials. Supporting Publications 2012:EN-139.
18. 21 CFR - Food and Drugs, Parts 170-199 - Chapter I, Subchapter B, Food for Human Consumption.
19. Zhang K, Wong JW, Begley TH, et al. 2012. Determination of siloxanes in silicone products and potential migration to milk, formula and liquid simulants. Food Addit Contam A. 29:1311-21.
20. Helling R, Kutschbach K, and Joachim Simat T. 2010. Migration behaviour of silicone moulds in contact with different foodstuffs. Food Addit Contam A. 27:396-405.
21. Helling R, Mieth A, Altmann S, et al. 2009. Determination of the overall migration from silicone baking moulds into simulants and food using ^{1}H-NMR techniques. Food Addit Contam A. 26:395-407.
22. Helling R, Seifried P, Fritzsche D, et al. 2012. Characterisation and migration properties of silicone materials during typical long-term commercial and household use applications: a combined case study. Food Addit Contam A. 29:1489-500.
23. Meuwly R, Brunner K, Fragnière C, et al. 2005. Heat stability and migration from silicone baking moulds. Mitt Lebensm Hyg. 96:281-97.
24. Simoneau C, Van den Eede L, and Valzacchi S. 2012. Identification and quantification of the migration of chemicals from plastic baby bottles used as substitutes for polycarbonate. Food Addit Contam A. 29:469-80.
25. Bouma K, Nab FM, and Schothorst RC. 2003. Migration of N-nitrosamines, N-nitrosatable substances and 2-mercaptobenzthiazol from baby bottle teats and soothers: a Dutch retail survey. Food Addit Contam A. 20:853-8.
26. Elskens M, Vloeberghs D, Van Elsen L, et al. 2012. Multiple testing of food contact materials: a predictive algorithm for assessing the global migration from silicone moulds. Talanta. 99:161-6.
27. Rosati JA, and Krebs KK. 2007. Emissions from cooking microwave popcorn. Crit Rev Toxicol. 47:701-9.
28. ECHA. 2013. Justification for the selection of a candidate CoRAP substance [http://echa.europa.eu/documents/10162/c98c53e1-7228-4985-8f87-6e202788106f]
29. ECHA. 2015. Community rolling action plan (CoRAP) update covering years 2015, 2016 and 2017. [http://echa.europa.eu/documents/10162/13628/corap_list_2015-2017_en.pdf]
30. Environment Canada & Health Canada. 2015. Screening assessment for the challenge trisiloxane, octamethyl- (MDM), Chemical Abstracts Service Registry Number 107-51-7. [https://www.ec.gc.ca/ese-ees/19584F14-D972-46A1-B71C-FA9A36FFB0FE/FSAR_MDM_EN.pdf]
31. Meeks RG, Stump DG, Siddiqui WH, et al. 2007. An inhalation reproductive toxicity study of octamethylcyclotetrasiloxane (D_4) in female rats using multiple and single day exposure regimens. Reprod Toxicol. 23:192-201.
32. Siddiqui WH, Stump DG, Plotzke KP, et al. 2007. A two-generation reproductive toxicity study of octamethylcyclotetrasiloxane (D_4) in rats exposed by whole-body vapor inhalation. Reprod Toxicol. 23:202-15.
33. Siddiqui WH, Stump DG, Reynolds VL, et al. 2007. A two-generation reproductive toxicity study of decamethylcyclopentasiloxane (D_5) in rats exposed by whole-body vapor inhalation. Reprod Toxicol. 23:216-25.
34. Quinn AL, Dalu A, Meeker LS, et al. 2007. Effects of octamethylcyclotetrasiloxane (D_4) on the luteinizing hormone (LH) surge and levels of various reproductive hormones in female Sprague-Dawley rats. Reprod Toxicol. 23:532-40.
35. Quinn AL, Regan JM, Tobin JM, et al. 2007. *In vitro* and *in vivo* evaluation of the estrogenic, androgenic, and progestagenic potential of two cyclic siloxanes. Toxicol Sci. 96:145-53.
36. He B, Rhodes-Brower S, Miller MR, et al. 2003. Octamethylcyclotetrasiloxane exhibits estrogenic activity in mice via ERα. Toxicol Appl Pharmacol. 192:254-61.
37. US EPA. 2005. Decamethylcyclopentasiloxane (D5): A 24-month combined chronic toxicity and oncogenicity whole body vapor inhalation study in Fischer-344 rats. [http://www.epa.gov/oppt/tsca8e/pubs/8ehq/2006/jan06/8ehq-0106-15273b_89060000174.pdf]
38. Environment Canada & Health Canada. 2008. Screening assessment for the challenge decamethylcyclopentasiloxane (D5), Chemical Abstracts Service Registry Number 541-02-6. [https://www.ec.gc.ca/ese-ees/default.asp?lang=En&n=13CC261E-1]
39. Environment Canada & Health Canada. 2008. Screening assessment for the challenge octamethylcyclotetrasiloxane (D4), Chemical Abstracts Service Registry Number 556-67-2. [https://www.ec.gc.ca/ese-ees/default.asp?lang=En&n=2481B508-1]
40. ECHA. 2012. D5 PBT/vPvB Evaluation. [http://echa.europa.eu/documents/10162/13628/decamethyl_pbtsheet_en.pdf]
41. Environment Canada & Health Canada. 2008. Screening assessment for the challenge dodecamethylcyclohexasiloxane (D6), Chemical Abstracts Service Registry Number 540-97-6. [https://www.ec.gc.ca/ese-ees/default.asp?lang=En&n=FC0D11E7-1]
42. Siloxane D5 Board of Review. 2011. Report of the Board of Review for Decamethylcyclopentasiloxane (D5). [http://www.ec.gc.ca/lcpe-cepa/default.asp?lang=En&n=515887B7-1&offset=1&toc=show]
43. Environment Agency. 2009. Environmental risk assessment report: decamethylcyclopentasiloxane. [https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/290565/scho0309bpqz-e-e.pdf]

44. Horii Y, and Kannan K. 2008. Survey of organosilicone compounds, including cyclic and linear siloxanes, in personal-care and household products. Arch Environ Con Tox. 55:701-10.

45. Tran TM, and Kannan K. 2015. Occurrence of cyclic and linear siloxanes in indoor air from Albany, New York, USA, and its implications for inhalation exposure. Sci Total Environ. 511:138-44.

46. Xu L, Shi Y, Wang T, et al. 2012. Methyl siloxanes in environmental matrices around a siloxane production facility, and their distribution and elimination in plasma of exposed population. Environ Sci Technol. 46:11718-26.

47. Dain JG, and Nicoletti J. 1995. Metabolic pathways of 4-[(3-methoxyphenyl)methyl]-2,2,6,6-tetramethyl-1-oxa-4-aza-2,6-disilacyclohexane (MPSC) hydrochloride, a silicon-containing xenobiotic, in rat, dog, and man. Xenobiotica. 25:951-61.

48. Lukasiak J, Dorosz A, Prokopowicz M, et al. 2005. Biodegradation of silicones (organosiloxanes). In: Biopolymers Online. A. Steinbüchel, ed., Wiley-VCH, Weinheim.

49. Enthaler S. 2014. Zinc-catalyzed depolymerization of end-of-life polysiloxanes. Angew Chem Int Ed Engl. 53:2716-21.

50. ECO U.S.A. 2015. Silicone recycling. [http://www.siliconerecycling.com/]

1-3 • **Important references for the preparation of this dossier. Information which is not explicitly supported by citations in the text was generally retrieved from at least one of these three sources.**