Characterisation of siloxanes in food contact

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Introduction

Food contact materials made from crosslinked polydimethylsiloxanes (PDMS) have a wide range of applications due to their properties (non-sticking effect, high temperature stability, flexible form) especially as baking moulds as well as coatings on baking paper. Non-crosslinked PDMS can be used in dependence of their molar masses as defoamers, lubricants and releasing agents in certain food production processes. Extractable siloxanes can be cyclic (D4, D5,...)*, linear (L3, L4,...)* or OH-terminated PDMS (* number of Si-O-units).

The aim of the present work was to characterise the composition of siloxanes that are intended for food contact. Investigations on the siloxane distribution pattern by HPLC-ELSD (D14 - D50) and GC-MS (volatile siloxanes) are carried out from two silicone oils (defoamers) and a releasing agent in comparison with extracts of crosslinked silicone elastomers, either from non- or post-cured baking moulds. Further investigations of silicone elastomers show the influence of temperature and time as well as the air flow on the desorption behaviour of siloxanes in a simulated post-curing process.

Summary

The total distribution of siloxanes reflects the potential migrants in direct food contact. Mainly higher-molecular siloxanes can be found in silicone oils, which have no significant absorption in the human GI (worst case calculated limit: D17). The distribution pattern shifts towards high-molecular siloxanes with increasing viscosity of the investigated silicone oils. Cyclic and linear siloxanes ≤ D20/L20 have been shown to migrate via gas phase in a simulated baking process (200°C, 1 h). In extracts of the investigated silicone elastomers exclusively cyclic siloxanes were detected. The industrial post-curing process (200°C, 4 h) decreases the amount of low-molecular siloxanes in baking moulds with a significant discrimination of the siloxanes ≤ D24. The post-curing is necessary to comply with the requirements for the volatile organic compounds (VOC) of 0.5 % (recommendation VX of the BfR). By this process, the proportion of VOC in the investigated material (layer thickness 1.9 mm) was reduced from 1.03 % to 0.38 %. The VOC-values were shown to decrease with increasing temperature, time and air flow in a simulated post-curing process.

Method of the characterisation

silicone oils, releasing agents	total distribution	dissolved in isooctane	HPLC-ELSD	siloxanes **D12** to **D50**
	volatiles	**Thermodesorption with cryo focussing**	GC-MS	siloxanes **D4** to **D20,** or **L4** to **L20**
non-/post-cured baking moulds (grounded)	extractables	Soxhlet-extraction 6 h, n-pentane	HPLC-ELSD	siloxanes **D12** to **D50**

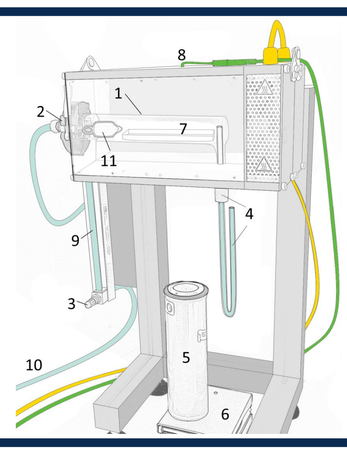

Fig. 1: Thermodesorption-furnace with cryo focussing (Fa. HTM Reetz GmbH)
1: sample chamber
2: gas connection (N_2, O_2)
3: flow valve
4: cooling trap
5: dewar vessel
6: lifting platform
7: aluminium shell for sample
8: temperature sensor
9: gas flow control
10: gas pipe
11: glas plug

Characterisation

Silicone oils (non-crosslinked PDMS)

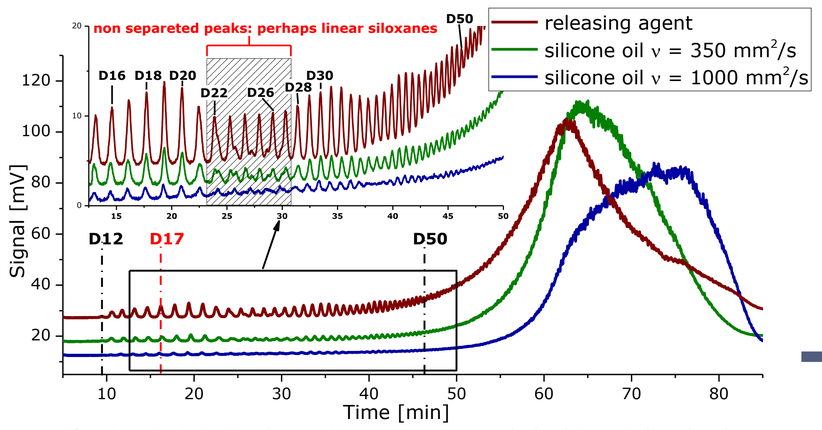

Fig. 2: HPLC-ELSD-chromatogram: non-crosslinked PDMS dissolved in isooctane (each time 10 g/l), D17 = 1260 Da limit (for silicon chemistry to comply with 1000 Da limit in carbon chemistry)

➡ HPLC-ELSD: total distribution
relevant for direct food contact

➡ total distribution of siloxanes from investigated samples:

- potential migrants in direct food contact
- major portion in non-crosslinked PDMS: higher-molecular siloxanes > D50
- siloxanes larger than D17 (worst case calculation): no significant absorption in the human GI
- with increasing viscosity: shift of the distribution pattern towards higher-molecular siloxanes (extended retention time)

➡ thermodesorbable siloxanes from investigated samples in a simulated baking process (200°C, 1 h):

- cyclic and linear siloxanes ≤ D20/L20 (potential migrants by gas phase transfer) in different amounts and conditions depending on the material

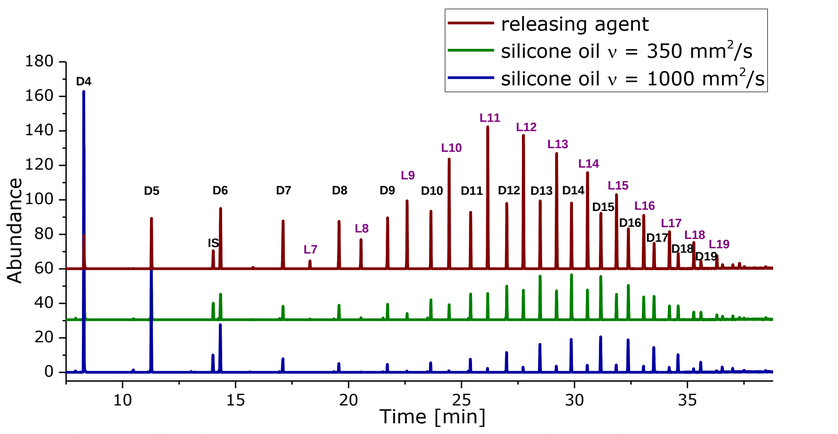

Fig. 3: GC-MS chromatogram: non-crosslinked PDMS after thermodesorption with cryo focussing, each time 1 g material, 200°C, 1 h, N_2-flow (30 ml/min), cooling agent: EtOH/liquid N_2

➡ GC-MS: distribution of volatile cyclic and linear siloxanes up to D20 or L20 depending on the thermodesorption conditions
relevant for gas phase transfer at baking processes

Elastomers (crosslinked PDMS)

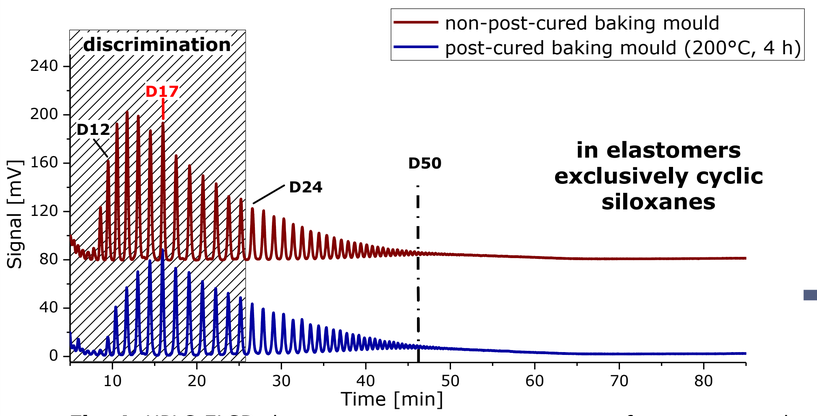

Fig. 4: HPLC-ELSD chromatogram: n-pentane extracts of non-post-cured and post-cured baking moulds (layer thickness: 1,9 mm)

➡ n-pentane extracts of the investigated baking moulds (layer thickness 1,9 mm):

- exclusively cyclic siloxanes
- by industrial post-curing process (200°C, 4 h, air flow: 120 ml/min/g silicone): significant discrimination of the siloxanes ≤ D24
- compared to non-crosslinked PDMS: no relevant amount of higher-molecular siloxanes > D50 in the extractables

➡ thermodesorbable siloxanes from investigated samples in a simulated baking process (200°C, 1 h):

- exclusively cyclic siloxanes (potentially relevant migrants)
- discrimination of cyclic siloxanes compared to non-post-cured baking moulds (same conditions)

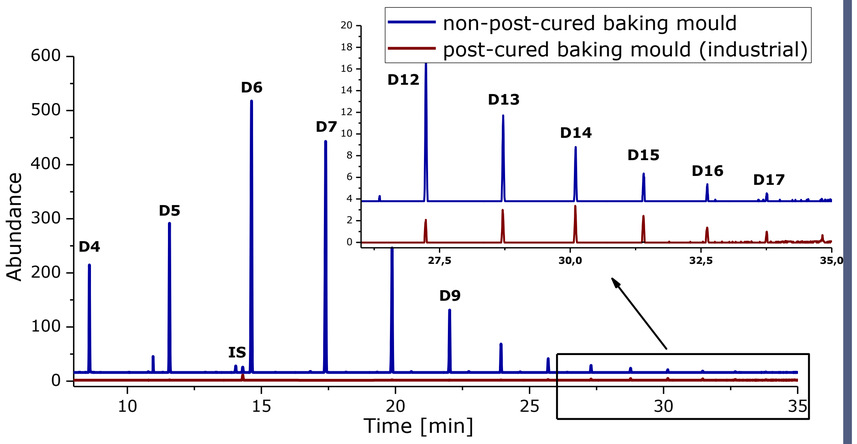

Fig. 5: GC-MS chromatogram after thermodesorption with cryo focussing: non-post-cured and post-cured baking moulds in a simulated baking process (200°C, 1 h)

Influence factors on a simulated post-curing process

simulated post-curing process of crosslinked PDMS in the thermodesorption-furnace at an air flow of 15 ml/min/g silicone and variable temperature and time conditions

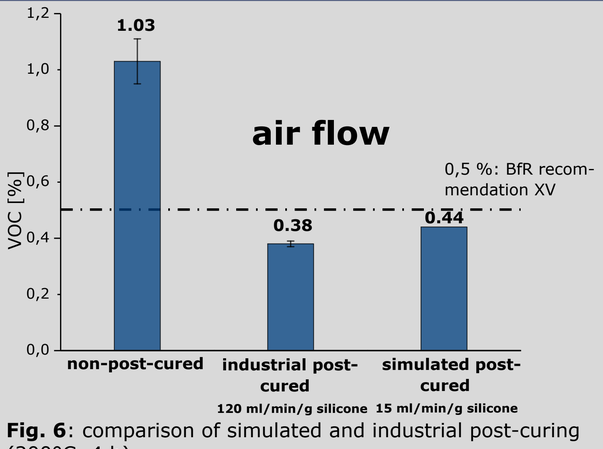

Fig. 6: comparison of simulated and industrial post-curing (200°C, 4 h)

➡ simulated post-curing less effective (due to lower air flow), comparable dimension
→ **applicability** of the simulation

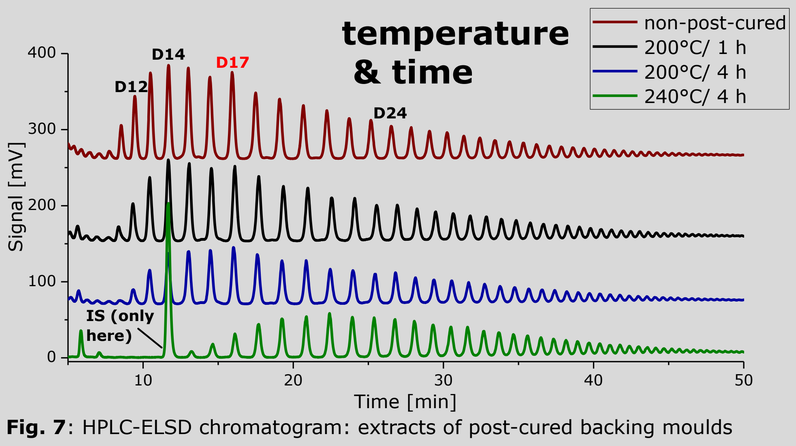

Fig. 7: HPLC-ELSD chromatogram: extracts of post-cured backing moulds

➡ decreasing content of lower-molecular siloxanes by simulated post-curing processes (≤ D24) depending on the conditions

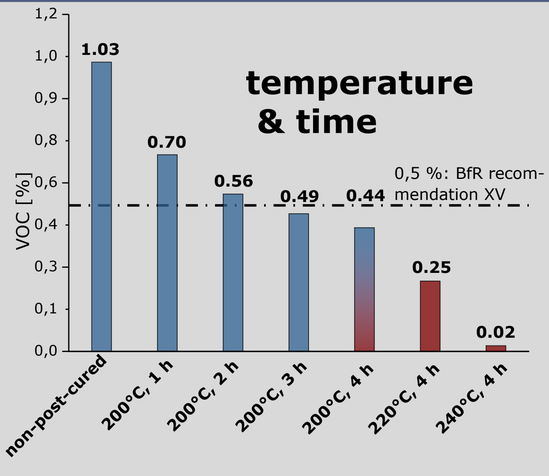

Fig. 8: impact on the VOC-values by different conditions (temperature [red bars], time [blue bars]) in the simulated post-curing process

➡ decreasing VOC-values as a function of temperature und time