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 patterns by HPLC-ELSD (D14 - D50) and GC-MS (volatile siloxanes) were carried out from two silicone oils (defoamers) and a releasing agent in connection 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.

Method of the characterisation
silicone oils, releasing agents total distribution volatiles non-post-cured baking moulds (grounded) extractables dissolved in isociane Thermodesorption with cryo focusing HPLC-ELSD siloxanes D12 to D50 Thermodesorption conditions: HPLC-ELSD chromatogram: non-crosslinked PDMS dissolved in isociane (each time 10 g). D14 = 1200 Da limit (for silicon chemistry to comply with 1000 Da limit in carbon chemistry). HPLC-ELSD: total distribution relevant for direct food contact

Characterisation
Silicone oils (non-crosslinked PDMS)

- 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)

thermoreolatile 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

Elastomers (crosslinked PDMS)
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

thermorevolatile 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)

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. 1: Thermodesorption-furnace with cryo focusing (H. HTM React GmbH).
1: sample chamber
2: gas connection (N2, O2)
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: Glenn plug

Fig. 2: HPLC-ELSD chromatogram: non-crosslinked PDMS dissolved in isociane (each time 10 g). D14 = 1200 Da limit (for silicon chemistry to comply with 1000 Da limit in carbon chemistry). HPLC-ELSD: total distribution relevant for direct food contact

Fig. 3: GC-MS chromatogram: non-crosslinked PDMS after thermodesorption with cryo focusing, each time 1 g material, 200°C, 1 h, N2-flow (30 ml/min), cooling agent: EEDQ/Et4N.

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

Fig. 4: HPLC-ELSD chromatogram: n-pentane extracts of non-post-cured and post-cured baking moulds (layer thickness 1.9 mm)

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

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

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 and time