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Heat stability and migration from silicone baking moulds

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Introduction

Flexible silicone baking moulds, available in different forms and colours, have been marketed for some years as alternatives to traditional metal bakeware. According to the manufacturers, silicone baking moulds offer numerous practical advantages: they are non-stick, can be used in the microwave, are dishwasher-safe and resistant to a large temperature range.

Silicones constitute a group of polymeric chemical substances containing polysiloxanes characterized by Si-O-Si and Si-C bonds. Silicones include a range of products with a variety of properties and applications: silicone liquids (release agents, impregnating agents for textiles, additives, etc.), silicone pastes (lubricants, etc.), silicone resins (heat-resistant and release coatings, etc.) and silicone elastomers (sealants, baking moulds, etc.).

Silicones, for food contact applications, are not regulated at the EU level but at the national level for example in Germany (1), France (2), etc. Annex 1 of the Regulation (EC) 1935/2004 includes Silicones within a list of materials and articles which may be covered in the future by specific measures (3). In Switzerland, there are no specific regulations for articles in silicones but they must fulfill the general requirements of the Swiss Ordinance concerning "Articles of Daily Use" (4) which states, as in the article 3 of the Regulation (EC) 1935/2004, that articles should not release to or form in foodstuffs any substance in a quantity that poses a risk to human health or that adversely affects the organoleptic properties of the food. The Council of Europe, in which Switzerland actively participates, issued "Resolution AP (2004) 5 on silicones used for food contact applications" which contains some specific requirements and an inventory list of substances used in the manufacture of the products (5). One requirement states: "The total of all substances migrating into food from silicone materials or articles should not exceed 10 mg/dm^2 of the surface

area of the final material or article or 60 mg/kg of food, this being considered as the overall migration limit". The same limit is given in the French legislation (2).

Even though silicone elastomers demonstrate a high degree of thermal stability and excellent resistance to aging, high temperatures lead to depolymerization of the elastomer, with subsequent volatilization and migration of certain substances. The few publications concerning the suitability of silicones as food contact materials have indeed shown that a certain quantity of substances migrates from silicone-based articles (6, 7).

The objective of this work was to study the release of chemical substances from the silicone baking moulds at various temperature, especially around 200–220 °C, temperatures attained in an oven when cakes and pastries are baked. Some tests at higher temperatures up to 280 °C were also performed to check the statement of the manufacturers concerning the heat stability of the moulds. The tests currently specified for migration for food contact applications involve temperatures not exceeding 175 °C. It is thus very important to develop migration procedures that make possible the investigation in a real temperature range.

The stability of the silicone moulds at high temperature was checked by two tests: measurement of the loss of volatile components during heating as described in the German recommendations (1) and the French legislation (2) and overall migration (OM) studies with modified polyphenylene oxide as a food simulant. Some indications about the nature of the migrants were also collected during this study.

Experimental

Samples

Silicone baking moulds of various shapes were received or bought from different retail stores (Table 1). These kitchenware are used in food preparation, especially for baking cakes, pastries, etc., in a microwave or in a conventional oven and for storage of food in the freezer. According to the manufacturers, the moulds can withstand extreme temperatures such as the ones reported in Table 1.

Table 1
Characteristics of silicone baking moulds samples

Sample Nr	*Type mould size (cm)*	*Temperature min/max (°C)*[1]	*Thickness (mm)*[2]	*Colour*
A	*4 Baking forms* 16×15×3	–25 to 220	1.97	Red
B	*12 Mini-Gugelhofs* 30×22.5×3.5	–25 to 250	1.17	Red
C	*4 Mini-puddings* 17×17×5.7	–60 to 260	1.39	Blue
D	*6 Muffins* 30×17.5×7	–40 to 280	0.95	Orange
E	*24 Minicakes* 60×40×3	–40 to 280	1.02	Black
F	*9 Minicakes* 60×40×3	–40 to 280	0.97	Red
G	*9 Minicakes* 30×17.5×3.5	–60 to 280	1.20	Red-brown

[1] according to the manufacturers
[2] average value, measured at different positions

Chemicals and apparatus

Modified polyphenylene oxide (MPPO, *Tenax,* temperature stability: T_{max}= 350 °C) 60 to 80 mesh (Supelco): before the first use MPPO was extracted 6 h with diethylether, transferred in a Petri dish which was placed in a fume hood to allow the diethylether to evaporate. The complete evaporation of the solvent was achieved by placing the Petri dish into an oven at 160 °C for 6 h. Dry MPPO was stored into a closed flask. Diethylether p.a. (Merck) was distilled over 1 g sodium hydride per liter diethylether. The samples were aged in an oven (Heraeus T 5042 EK) without air circulation. The oven was regulated within the permitted tolerance (±5 °C) on the temperature indication given by an additional thermocouple (type K) positioned in the middle of the oven at the sample location. The temperature profile of each experiment was recorded by a datenlogger (Ecolog TN4 with an accuracy of ±0.6 °C at 200 °C).

GC-MS analyses were performed using a Hewlett-Packard GC 5890 equipped with an HP 5972 MSD detector. The capillary column was a DB-1ht (J & W Scientific) with the dimension 30 m×0.25 mm i.d. and a coating film thickness of 0.1 µm. The GC initial settings were: injector temperature 270 °C and column temperature 70 °C followed by a temperature program of 20 °C/min up to 360 °C. The mass spectrometer was operated at a transfer line temperature of 280 °C with EI at 70eV at a scan mass-range 50–400 amu. For spectra interpretation a Wiley 7 library was used.

MALDI-TOF/MS spectra were obtained from Solvias AG, 4002 Basel, using an LDI-1700 spectrometer (Linear Scientific, Inc. Reno, USA) equipped with a laser operating at 337 nm. The matrix used was 2,5-dihydroxybenzoic acid. The mass-range was 10000 Da (4 calibrating substances from 1300 Da to 7000 Da) with a mass accuracy of ±0.1 %. Single charged ions ($[M+Na]^+$) were detected and analyzed.

Overall migration at high temperatures

According to the Resolution of the Council of Europe (5), migration tests should be conducted according to the EC Plastic Directives. The overall migration tests of the silicone baking moulds were performed according to the Commission Directive 97/48/EC laying down the basic rules necessary for testing migration of the constituents of plastic materials and articles intended to come into contact with foodstuffs (8). The experimental methods are described in the European Standard EN 1186-13: "Test methods for the determination of the overall migration at high temperatures" (9). The determination of the overall migration into fatty food simulants from plastic material articles is performed by total immersion of test specimens in a fatty food simulant, normally olive oil, at temperatures up to 175 °C for selected times. At high temperature the migration tests with olive oil introduce a number of analytical difficulties (oxidation of oil, ...). Replacement of olive oil by an appropriate absorbent material is an alternative accepted by the legislation: MPPO is listed like isooctane and ethanol as a test medium in substitute fat test (8). In this substitute procedure, the mass of the components absorbed on modified polyphenylene oxide (MPPO) is taken as the measure for the assessment of the overall migration into a fat simulant. This procedure with MPPO has allowed to test silicone baking moulds up to 280 °C, maximum temperature according to the manufacturers of the heat stability of some articles.

When an article is intended to come into repeated contact with foodstuffs like these silicone baking moulds, tests shall be carried out three times (M1, M2 and M3) on a single sample using a fresh sample of simulant on each test as described in the European Standard EN 1186-1: "Guide to the selection of conditions and test methods for overall migration" (10). Its compliance shall be checked on the basis of the level of the migration found in the third test (M3).

The residue of the migration was analyzed by GC-MS and MALDI-TOF to investigate the nature of the migrants.

Principle

The surface of the sample to be tested was covered with modified polyphenylene oxide (MPPO) and kept at the selected time/temperature test conditions in an oven. The MPPO were then extracted with diethylether. The extract was evaporated to dryness using a nitrogen stream and the residue mass was determined gravimetrically. The residual mass does not contain volatiles.

Sample preparation

The determination of the overall migration of silicone baking moulds was performed on the flat bottom part of the article in contact with the food. The dust on the samples was removed with compressed air and the samples were treated with antistatic cloth.

Procedure

The surface of the sample to be tested was covered with MPPO taking 4 g MPPO per dm^2 of surface area. For the blank determination, an empty Petri dish was taken and the same mass of MPPO was placed on it. The examination of a blank was carried out in parallel. The test sample was covered with a glass plate and put in the preheated oven at the required temperature. The sample was left in the oven for the selected period of time (M1, 1 h in general) as soon as the temperature in the oven had once again reached a temperature within the permitted tolerance (±5 °C) for the test temperature. The average time for the oven to reach the test temperature again was 13 min at 175 °C, 16 min at 220 °C, 23 min at 260 °C and 27 min at 280 °C. The sample was removed from the oven and allowed to cool to room temperature without removing the glass cover. The MPPO was carefully transferred into a 200 ml Erlenmeyer flask and 20 ml of diethylether was added. The solution was stirred for 1 minute and then allowed to stand for 1 minute without shaking. The diethylether solution was decanted from the MPPO through a filter into a 200 ml vial. The extraction procedure of MPPO was repeated twice with each time 30 ml diethylether. The filter was rinsed with 10 ml diethylether and the combined diethylether solution was concentrated with a Rotavap to approximately 5 ml. The residue was transferred to a weighted 15 ml vial and concentrated further to dryness, using a stream of nitrogen until constant weight was obtained. The mass of the residue was determined by substracting the original mass of the vial from the mass of vial plus residue.

The second migration test (M2) was performed with the sample used for the first test via the same procedure as described above. The third migration test (M3) was performed with the sample used for the first and the second tests via the same procedure. Prolonged heating time tests were performed on two samples to check the effect of a repeated use on the overall migration. Again the overall migration value during a repeated 1 h test at the selected temperature was determined during 100 hours. The sample was heated with MPPO for (x-1) h, MPPO was discarded, a fresh sample of MPPO was taken and the sample was heated for a further 1 h. The migrants in the fresh MPPO were determined to give the overall migration value for 1 h at time x.

The precision of the measurements was assessed on different samples at 220 °C. This was shown to be sample dependent. The standard deviation under repeatability conditions oscillated between 12–28 % for the first migration test (M1) and decreased steadily for each additional heating cycle to reach 6–15 % for the third migration test (M3).

Volatiles

The total release of volatile substances was measured by simply weighing the moulds before and after the heating during 4 hours at 200 °C as described in the German recommendations (1) and the French legislation (2). About 10 g of the sam-

ple were cut in pieces of about 1×2 cm and left for 48 h above calcium chloride in a desiccator. The pieces were weighed (precision of ±0.1 mg) and then put in the oven for 4 h at 200 °C. After cooling in a desiccator the pieces were weighed again and the percentage of volatiles was calculated based on the ratio of the weights. The release of volatiles should not exceed 0.5 % (1, 2).

Results and discussion

Overall migration

The determination of the overall migration of the sample A was performed at different temperatures during repeated 1 h contact cycle with MPPO (Figure 1). Up to 100 °C the sample showed low migration value, especially at the third 1 h exposure. From 150 °C, the values increased rapidly for the three exposure time and the limit of 10 mg/dm² prescribed by the Resolution of the Council of Europe (5) is reached in most cases. These results confirm the good stability of silicone elastomers up to 150 °C. All experimental points can be fitted with a sigmoidal curve of the type:

$$M_T = \frac{K}{(1 + b \cdot e^{-R \cdot T})}$$

where T is the temperature of observation in degree Celsius, R depicts a degradation rate of the silicone, K and b are two constant factors. The curve in Figure 1 shows the amount of migrants liberated by sample A at the third 1 h exposure test (M3) used to check the compliance of articles intended to come into repeated contact with foodstuffs.

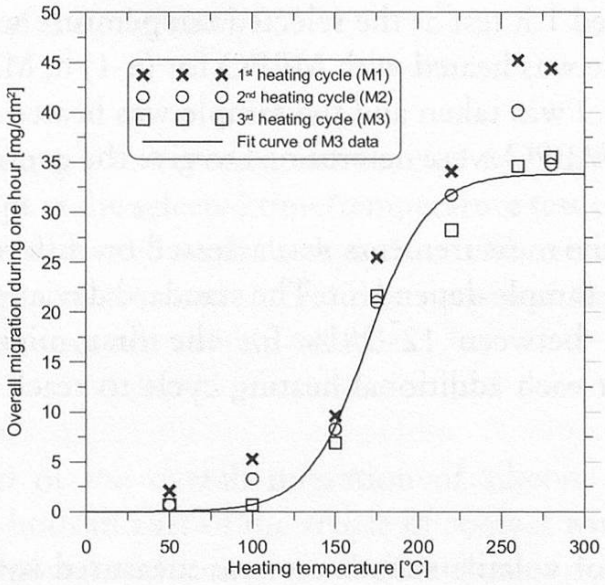


Figure 1 **Overall migration of sample A during a repeated one hour test**

The thermal stability of the different samples was tested at temperature between 175 and 280 °C (Table 2). At 175 °C for the first 1 h contact all the investigated samples showed high overall migration values, between 25.5 mg/dm² and 49.2 mg/dm². At the third exposure the values M3 used to check the compliance of articles intended to come into repeated contact with foodstuffs were slightly lower. Again no significant difference was observed between the samples. The increase of the test temperature from 175 to 220, 260 and 280 °C showed in parallel a slight increase of the migration values. The behavior of the various samples at these temperatures was almost the same. The true values for the overall migration in fatty food simulants are subject to uncertainty owing to the lack of precision inherent in the method. A point to consider is that at high temperatures, the more volatile compounds of the migrate could evaporate without being absorded on the MPPO and consequently could not contribute to the overall migration value. The values in Table 2 possibly underestimate the real loss of material during the heating.

Table 2
Overall migration during a repeated one hour test at different temperatures

Sample	*A* *mg/dm²*	*B* *mg/dm²*	*C* *mg/dm²*	*D* *mg/dm²*	*E* *mg/dm²*	*F* *mg/dm²*
T=175 °C						
M1	25.5	25.9	29.1	49.2	33.8	25.8
M2	21.1	25.7	21.6	33.7	26.1	19.7
M3	21.8	21.8	23.9	31.7	23.2	17.7
T=220 °C						
M1	34.2	44.7	38.2	48.1	41.5	33.7
M2	31.8	41.9	33.4	37.2	36.0	32.1
M3	28.4	35.9	28.9	32.8	41.9	29.0
T=260 °C						
M1	45.3	42.7	40.9	44.7	50.5	37.7
M2	40.3	45.1	32.6	40.5	48.2	33.7
M3	34.7	31.8	27.2	27.9	34.1	24.9
T=280 °C						
M1	44.4	40.7	41.5	45.0	44.0	37.2
M2	32.1	33.5	38.4	39.0	37.6	32.3
M3	32.8	31.6	39.6	31.3	34.9	27.3

M1: Sample X heated 1 h (X1)
M2: Sample X1 heated 1 h (X2)
M3: Sample X2 heated 1 h (X3)

The values of the overall migration during a 1 h heating cycle at 220 °C based on the heating time of samples A and D are depicted in Figure 2a. These values give an indication of the quantity of the migrants liberated each time the mould is heated for 1 h at 220 °C. The values of the overall migration decrease rapidly during the first exposure of the moulds with MPPO. But even after 100 h of heating, a small quantity of substances continue to migrate from the moulds to the MPPO. This certainly indicates a continual degradation (depolymerization) process which always supplies

new substances able to migrate. Mould A is two times thicker than mould D; this certainly plays a role in the quantity of the products of decomposition and thereafter in the quantity of the migrants. The data were not corrected as regards the thickness of the samples in order to depict effective migration values. By plotting the measured values as the sum of the measured migration in function of the square root of time (Figure 2b) it appears clearly that the loss is not linear. This indicates that the kinetics of loss is not principally governed by a diffusion process. Other processes, such as the degradation rate of the silicone backbone or the direct volatilization of migrants at the sample surface are likely to play a role in this measurement.

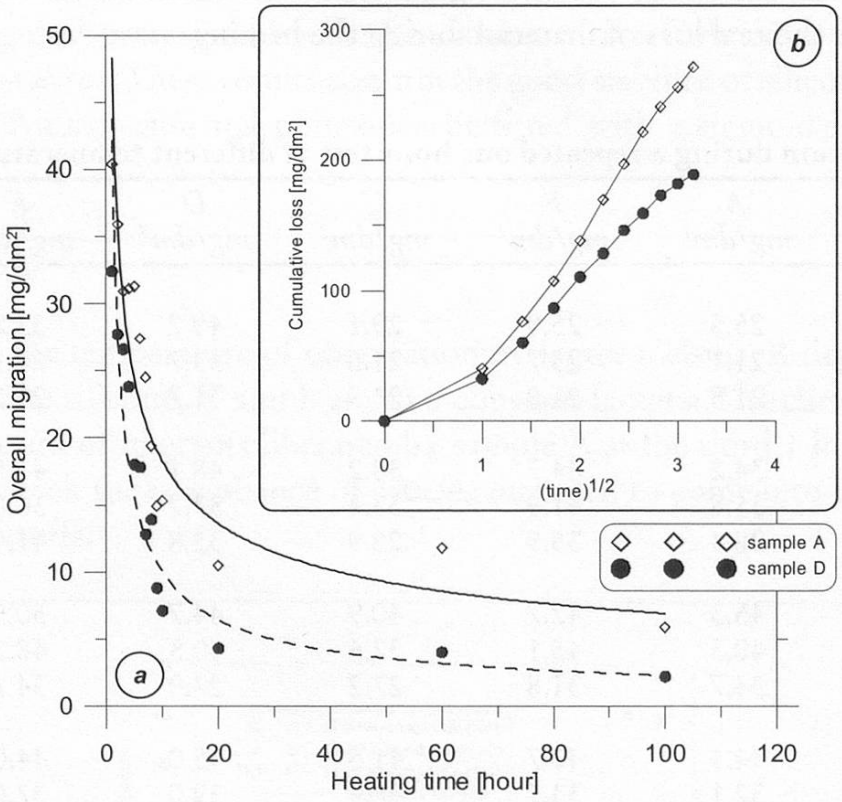


Figure 2 **Overall migration during one hour test at 220 °C after a prolonged heating time**

The results do not take into account the "simulant D reduction factor" used to correct the results for foodstuffs containing fat as indicated in Directive 85/572/EEC (11). For example a reduction factor of 3 would apply for confectionery products in paste form with fatty substances on the surface and a reduction factor of 5 for fresh pastry, cakes and other baker's wares with fatty substances on the surface. At all temperatures, even at 280 °C at the third 1 h exposure contact and when a reduction factor of 5 is used, all the investigated silicone baking moulds had an overall migration value below the recommended limit of 10 mg/dm² (5).

Volatiles

The total release of volatile substances after 4 h at 200 °C (Table 3) was measured by weighing the moulds before and after the heating as described in the German recommendations (1) and the French legislation (2). During the first heating cycle of 4 h at 200 °C, the weight loss of the samples was 0.11–1.78 %. As shown in Table 3 the values of the weight loss decrease rapidly after the first heating cycle. Already during the second and during the whole of the following heating cycle, all the samples showed a value lower than 0.21 %, below to the limit of 0.5 % given in the German and French recommendations. The high weight loss in the first heating cycle is most likely due to residual solvents and/or by-products formed during the manufacture of the articles or due to the fact that the time for the postcuring of the article was not sufficient. This process is easy but requires much energy. To avoid additional expenses, some firms leave out this last stage and ask their customers to heat the mould at 230 °C during 2 h without food before the first use, stating that the possible development of some smoke is not deleterious.

Table 3
Weight loss of volatiles (%) at 200 °C in heating cycles of 4 h

	Number of heating cycle			
Sample	*1×*	*2×*	*3×*	*5×*
A	0.11 ± 0.01*	0.04 ± 0.01	0.02 ± 0.01	0.01 ± 0.01
B	0.58 ± 0.01	0.12 ± 0.01	0.08 ± 0.01	0.04 ± 0.01
C	0.93 ± 0.01	0.15 ± 0.00	0.07 ± 0.01	0.04 ± 0.01
D	1.68 ± 0.02	0.20 ± 0.02	0.11 ± 0.03	0.06 ± 0.04
E	0.96 ± 0.04	0.21 ± 0.03	0.15 ± 0.02	0.08 ± 0.01
F	1.78 ± 0.02	0.07 ± 0.03	0.14 ± 0.03	0.12 ± 0.09
G	0.46 ± 0.01	0.12 ± 0.00	0.06 ± 0.01	0.04 ± 0.01

* average of three measurements with the standard deviation s

By varying the temperature from 200 to 220 and then to 280 °C (Tables 3–5), the increase of the weight loss is considerable. Table 5 shows that the least stable sample D lost 4.47 % of its weight during the first 4 h of heating at 280 °C and even 1.44 % during the 5th heating cycle of 4 h. These results show a strong dependence of the amount of volatiles on the heating temperature and clearly indicate that these silicone moulds are not as stable at high temperature as advertised by their manufacturers. The sample D, supposed to withstand temperature to 280 °C, lost during the first 12 h of heating (3×4 h heating cycle) 1.99 % of its weight at 200 °C, 2.38 % at 220 °C and even 8.58 % at 280 °C. After these prolonged thermal treatments, some samples were discolored or brittle.

Table 4
Weight loss of volatiles (%) at 220 °C in heating cycles of 4 h

	Number of heating cycle			
Sample	*1×*	*2×*	*3×*	*5×*
A	0.15 ± 0.01*	0.06 ± 0.01	0.05 ± 0.01	0.02 ± 0.01
B	0.74 ± 0.02	0.17 ± 0.01	0.10 ± 0.01	0.02 ± 0.01
C	1.21 ± 0.03	0.14 ± 0.02	0.10 ± 0.03	0.08 ± 0.01
D	2.11 ± 0.06	0.19 ± 0.01	0.08 ± 0.02	0.08 ± 0.03
E	1.37 ± 0.09	0.19 ± 0.05	0.14 ± 0.03	0.11 ± 0.01
F	1.86 ± 0.08	0.17 ± 0.03	0.14 ± 0.02	0.16 ± 0.03
G	0.65 ± 0.02	0.13 ± 0.01	0.08 ± 0.01	0.05 ± 0.01

* average of three measurements with the standard deviation s

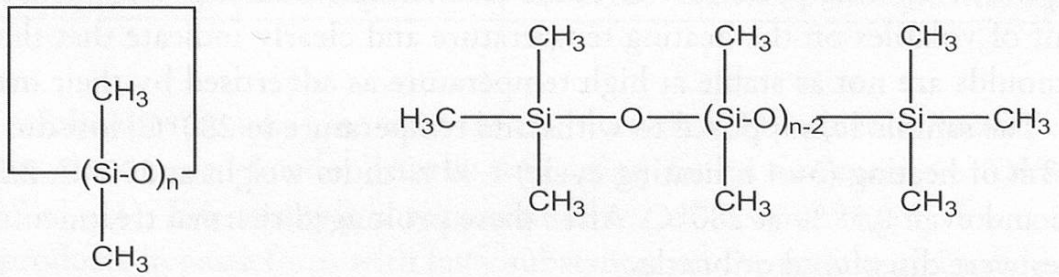
Table 5
Weight loss of volatiles (%) at 280 °C in heating cycles of 4 h

	Number of heating cycle			
Sample	*1×*	*2×*	*3×*	*5×*
A	0.78 ± 0.08*	0.30 ± 0.02	0.28 ± 0.04	0.25 ± 0.02
B	3.01 ± 0.11	2.24 ± 0.01	2.23 ± 0.21	1.34 ± 0.22
C	4.11 ± 0.25	2.87 ± 0.18	1.70 ± 0.21	0.63 ± 0.01
D	4.47 ± 0.22	2.25 ± 0.48	1.86 ± 0.37	1.44 ± 0.38
F	3.27 ± 0.07	1.51 ± 0.08	1.40 ± 0.09	1.95 ± 0.07

* average of three measurements with the standard deviation s

Characterisation of the migrants

Silicone baking moulds are silicone elastomers made from crosslinked polydimethylsiloxanes. Thermal degradation of silicone elastomers have been described in many studies (12–15). The decomposition of the polymers occurs in three stages: 1) evaporation of volatile components, 2) thermal decomposition and 3) thermal oxidation: The second and third processes often overlap. Additives and initial removal of volatiles by postcuring increase the stability (16).



Cyclic polydimethylsiloxanes (Cn)
n=5–35 $Si(CH_3)_2$-groups

Linear polydimethysiloxanes (Ln)

Figure 3 **Structure of the migrants**

According to the literature, the degradation products consist primarily of cyclic polydimethylsiloxane (Cn) and linear polydimethylsiloxane (Ln) oligomers (Figure 3). It is assumed that linear polydimethylsiloxanes are methyl terminated linear chain without excluding the fact that some chains are hydroxyl terminated (17, 18).

The distribution of the different siloxanes in the residue of the global migration at different temperatures were determined from the MALDI-TOF and the GC-MS. In the MALDI-TOF, the oligomeres have a difference of 74.2 Dalton which is the mass of the repeated unit $Si(CH_3)_2O$-group. The migrating substances mainly con-

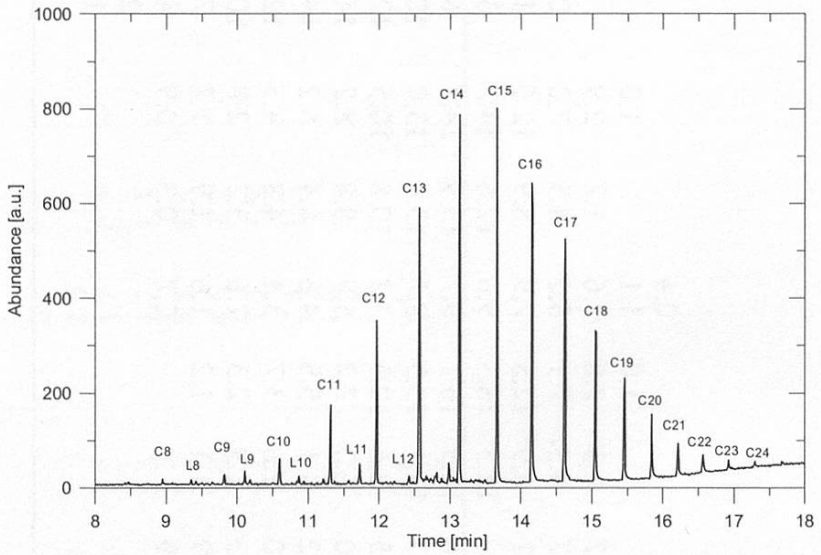


Figure 4 **GC-MS of residue of sample A at the third one hour exposition at 175 °C**

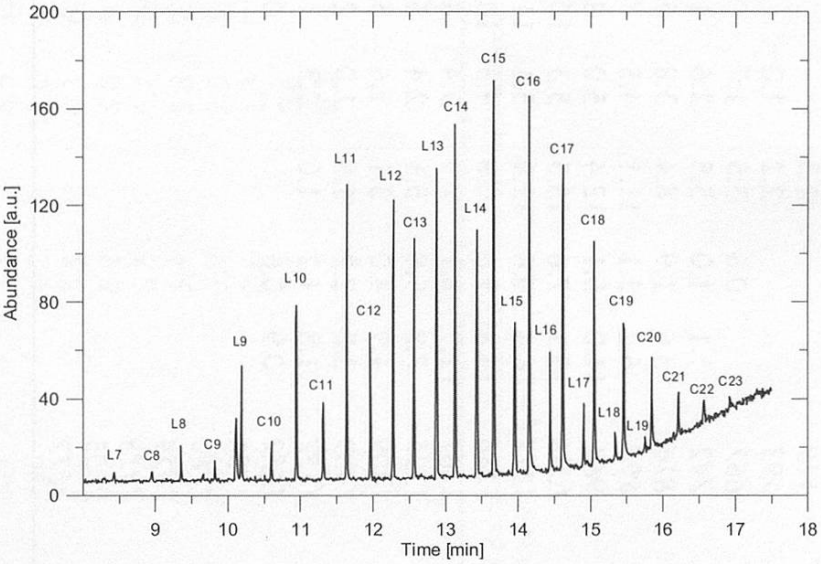


Figure 5 **GC-MS of residue of sample B at the third one hour exposition at 175 °C**

Table 6
Composition of residue in % from the overall migration tests

Temp.		*175 °C*						*220 °C*						*260 °C*					
Sample		*A*	*B*	*C*	*D*	*E*	*F*	*A*	*B*	*C*	*D*	*E*	*F*	*A*	*B*	*C*	*D*	*E*	*F*
Cn	*MW*																		
C7	*519*			1.3															
C8	*593*			2.2	1.0		1.1												
C9	*667*		0.6	3.5	1.7		2.9												
C10	*742*	1.1	1.0	5.5	2.6	1.2	5.6												
C11	*816*	3.6	1.9	8.4	3.8	3.1	8.7				0.4								
C12	*890*	6.2	3.1	11.1	4.5	7.3	11.0			1.0	1.1		1.0						
C13	*964*	11.0	5.1	12.4	5.0	8.8	12.2	1.7	1.3	2.8	2.6	1.7	2.9						
C14	*1038*	15.1	7.6	13.5	5.3	10.4	13.1	4.7	4.3	7.1	5.2	4.5	7.0	0.5			0.5		
C15	*1112*	16.4	9.6	12.9	5.1	11.3	12.7	9.1	8.9	12.8	7.9	8.9	12.0	1.4		0.9	1.4		
C16	*1186*	14.8	9.6	10.6	4.3	10.6	10.7	13.4	12.3	16.3	9.6	12.6	14.7	3.2	1.5	2.1	3.3	0.6	1.0
C17	*1261*	11.9	8.1	7.9	3.4	8.3	8.2	15.6	12.9	16.1	9.7	13.9	14.7	6.4	3.2	4.3	6.7	1.7	3.0
C18	*1335*	7.8	5.8	5.1	2.4	5.5	5.8	14.7	11.1	13.3	8.7	13.4	13.0	10.0	6.2	8.2	10.3	4.0	6.7
C19	*1409*	4.9	4.0	3.1	1.6	3.5	3.8	12.5	8.6	10.3	7.2	10.8	10.5	12.7	10.2	12.4	12.7	8.0	11.7
C20	*1483*	3.2	2.2	1.8	1.0	2.2	2.3	10.0	6.0	7.7	5.8	8.8	8.2	14.3	14.0	15.3	13.0	12.9	15.2
C21	*1557*	1.8	1.2	1.0	0.5	1.1	1.3	7.2	4.1	5.5	4.6	6.4	6.2	14.2	14.6	16.1	11.6	15.4	16.1
C22	*1632*	0.9	0.6			0.5	0.7	5.0	2.6	3.7	3.4	4.8	4.3	12.3	11.9	14.0	9.6	16.6	14.4
C23	*1706*							3.3	1.9	2.3	2.6	3.2	2.8	10.0	11.6	11.3	7.4	14.3	11.6
C24	*1780*							1.9	1.1	1.2	1.6	1.9	1.7	7.2	7.5	7.2	5.2	11.5	8.5
C25	*1854*							0.9			0.7	0.9	0.9	4.4	3.7	4.3	3.2	7.2	5.4
C26	*1918*													2.4	2.6	2.7	1.6	4.4	3.3
C27	*2003*													1.2	1.9	1.2	0.9	2.3	1.9
C28	*2077*																	1.3	1.2

Temp.		*175 °C*						*220 °C*						*260 °C*					
Sample		*A*	*B*	*C*	*D*	*E*	*F*	*A*	*B*	*C*	*D*	*E*	*F*	*A*	*B*	*C*	*D*	*E*	*F*
Ln	*MW*																		
L7	*533*				1.6														
L8	*607*		0.7		4.4														
L9	*681*		2.3		8.5	1.6													
L10	*756*		4.2		11.0	3.3					0.7								
L11	*830*		5.5		10.3	6.8					1.6								
L12	*904*		6.2		8.0	5.5			1.3		3.1	0.7							
L13	*978*		6.3		5.7	3.9			3.3		4.7	1.3							
L14	*1052*		5.4		3.8	2.7			5.2		5.1	1.8					0.5		
L15	*1126*		3.9		2.3	1.7			5.4		4.6	2.0			0.4		1.0		
L16	*1200*		2.6		1.3	0.9			4.1		3.5	1.5			1.1		1.8		
L17	*1275*		1.4		0.6				2.8		2.4	1.0			1.4		2.4		
L18	*1349*		0.7		0.3				1.6		1.6				2.1		2.5		
L19	*1423*		0.5						0.8		1.0				2.1		2.1		
L20	*1497*								0.4		0.6				1.6		1.4		
L21	*1571*								0.3		0.2				1.6		1.0		

Cn = cyclic polydimethylsiloxane, Ln = linear polydimethylsiloxane
n = number of $Si(CH_3)_2$-groups

sist of siloxane oligomers of molar mass between 500 and 2100 Dalton which correspond to oligomers with 7 to 28 $Si(CH_3)_2O$-groups. Figures 4 and 5 represent typical GC-MS graphs of the residue of the global migration. Figure 4 represents the GC-MS obtained with sample A, mostly cyclic polydimethylsiloxane oligomers, at the third one hour exposition (M3) at 175 °C whereas Figure 5 represents sample B, mixture of cyclic and linear polydimethylsiloxane oligomers, at the same condition. Samples C, F and G show the same pattern as sample A whereas sample D and E, to some extent, are comparable to sample B.

The composition of the residue at the third one hour exposition (M3) in fonction of the temperature is given in Table 6. The GC-MS of the residue of the samples at different temperatures were normalized by considering that the total surface of all silicone peaks equals 100 %. The sum of cyclic (Cn) and linear (Ln) polydimethylsiloxane oligomers for some samples differ slightly from 100 % due to the fact that the percentage of each peak is only given to the first decimal.

By increasing the temperature during the test for the global migration, the size of the siloxane oligomers increases. From 175 °C to 220 °C and finally to 260 °C, the largest peaks for the sample A increase from n=14–16 to n=16–18 and n=19–21 units of $Si(CH_3)_2O$-groups. By increasing also the temperature from 175 to 220 and finally to 260 °C, the content of the linear polydimethylsiloxane oligomers in the residue decreases, for exemple from 39.7 % to 25.2 and then 10.3 % for sample B.

Compounds with a molecular weight above 1000 Dalton are commonly considered to be of low toxicological relevance because they can not normally enter the metabolism. The percentage of the polydimethylsiloxanes lower than 1000 Dalton varies from 21.9 to 68.1 % at 175 °C, between 1.7 and 14.2 % at 220 °C, whereas at 260 °C all the polydimethylsiloxanes in the residues are superior to 1000 Dalton. Two points could play an important role in this topic; at high temperatures: a) the thermal degradation of silicone elastomers favours the formation of larger oligomers and/or b) the lower oligomers are not absorbed by MPPO.

Conclusion

Up to 100 °C, silicone elastomeres can be considered as inert as shown by low overall migration values. Around 150 °C, silicone elastomers start to degrade at such a rate that the limit of 10 mg/dm^2 prescribed in the Resolution of the Council of Europe is reached in most cases. To keep the value within the limit, it is necessary to take into account the "simulant D reduction factor". Due to analytical uncertainty, there is no significant difference in the overall migration results of the various silicone baking samples. A study has shown that MPPO generally overestimates the contamination of the foods from packaging (19). The release of volatiles is high during the first use and then decreases rapidly.

Neither the determination of the overall migration, nor that of the volatiles gives a complete view of the behaviour at high temperature of the silicone moulds. Each one brings some part of the response to the thermal stability of silicone elastomers.

Some questions concerning the reality of the high temperature migration testings are still open. What is the real temperature at the food-silicone baking moulds interface especially in the case of food containing a certain quantity of water? What is the temperature of the paste or the cake in a normal or a microwave oven? These questions are very significant due to the fact that increasing the temperature accelerates the rate of the degradation process of the moulds. The migration levels in foods compared to MPPO is another critical point. It is therefore intended to investigate further the migration study with real foods instead of simulants.

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Summary

Heat stability of silicone baking moulds used in bakery has been evaluated with different standard methods. The results of the migration tests using modified polyphenylene oxide (MPPO, Tenax) as a food simulant indicate that these materials are stable up to 150 °C. Above this temperature the limit of 10 mg/dm² prescribed by the Resolution of the Council of Europe is reached in most cases. The migration residue is essentially composed of cyclic oligomeric polydimethylsiloxanes, however, some samples contain cyclic and linear oligomeric polydimethylsiloxanes. The mass of these oligomeres is between 500 and 2100 Dalton whereas the maximum varies from 1000–1500 Dalton depending on the test temperature. The loss of volatiles at 200 °C completes the migration values and shows that some moulds lose more than 0.5 % of their weight during a 4 hour heating process. Although the loss of the mould weight decreases rapidly with the number of uses, all the observations indicate that silicone baking moulds are not inert enough for use in all the range of temperature indicated by the manufacturers.

Zusammenfassung

Die Temperaturbeständigkeit von Silikonbackformen wurde mit verschiedenen genormten Methoden überprüft. Die Ergebnisse der Globalmigrationsprüfung mit modifiziertem Polyphenylenoxid (MPPO, Tenax) als Lebensmittelsimulanz hat ergeben, dass das Material bis 150 °C stabil bleibt. Ab dieser Temperatur überschreiten fast alle geprüften Muster den Globalmigrationsgrenzwert von 10 mg/dm², der von dem Europarat empfohlen wird. Der Hauptanteil des Migrationsrückstandes besteht aus zyklischen oligomeren Polydimethylsiloxanen, und in einigen Mustern sind auch lineare vorhanden. Diese Oligomere haben Molekularegewichte zwischen 500 und 2100 Dalton, wobei der Hauptanteil je nach Testtempereratur zwischen 1000–1500 Dalton variiert. Die Bestimmung der flüchtigen Anteile bei 200 °C vervollständigen die Globalmigrationresultate, teilweise betragen die Gewichtsverluste während des Erhitzens nach 4 Stunden mehr als 0.5 %. Obschon der Gewichts-

verlust der Silikonbackformen mit zunehmenden Gebrauch exponentiell abnimmt, zeigen alle Experimente, dass, entgegen den Angaben der Hersteller, die Silikonbackformen über den ganzen Temperaturbereich nicht genügend inert sind.

Résumé

La stabilité thermique des moules en silicone utilisés en pâtisserie a été étudiée à l'aide de diverses méthodes types. Les résultats des essais de migration utilisant de l'oxide de polyphénylène modifié (MPPO, Tenax) comme simulant alimentaire indiquent que ces matériaux sont stables jusqu'à 150 °C. Au-dessus de cette température, la valeur de 10 mg/dm^2 recommandée par la Résolution du Conseil de l'Europe est atteinte dans la plupart des cas. Le résidu de migration est composé principalement d'oligomères de polydiméthylsiloxane cycliques mais également linéaires pour certains moules. Ces oligomères ont une masse comprise entre 500 et 2100 Dalton avec un maximum qui varie de 1000–1500 Dalton avec la température de test. La mesure de perte des substances volatiles à 200 °C complète les résultats de migration et montre que certains moules perdent plus de 0.5 % de leur poids durant un chauffage de 4 heures. Bien que la perte de masse des moules diminue rapidement avec le nombre d'utilisation, toutes les observations indiquent que les moules de cuissons en silicone ne sont pas assez inertes pour une utilisation dans tout le domaine des températures annoncées par les fabricants.

Key words

Silicones, baking moulds, heat stability, migration, volatiles

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