Guidelines on Compliance Testing for Silicone Elastomers

1. Scope

This chapter applies to the determination of the overall migration from Silicone elastomers in contact only with fatty food for which the testing procedures under Regulation (EU) N°10/2011 are inappropriate and which formally do not apply due to the exemption of silicones from this legislation. The following examples on use are representative but not limiting to existing applications: household articles like baking molds, containers (squeezable storage bottles) bottles but also closures or membranes used in food packaging and processing

2. Definitions

Silicone elastomers are manufactured from siloxane pre-polymers with some functional groups like vinyl-, hydrogen- or hydroxyl- which are crosslinked in the presence of low levels of catalysts . As a result, Silicone elastomers are three-dimensionally chemically cross-linked Polydimethylsiloxanes which within a broad temperature range can be substantially deformed under stress but recover quickly to near its original shape when the stress is removed. The finished chemically cross-linked product cannot be dissolved in organic solvents but typically swells to a certain extend. Material shaping cannot be performed anymore once the chemical cross-linking has taken place. As silicones are very stable towards light, humidity and other environmental influences, fillers are needed to improve the mechanical properties but no further additives like antioxidants, organic plasticizers or other further stabilizers are needed.

Hence, silicone elastomers are very different from plastics not only related to their physico-chemical characteristics, but also to their manufacturing procedure.

3. Material Specific Properties to be considered when testing this class of FCM

a. Brief outline as to why plastic testing guidelines may be inappropriate

Since silicone elastomers are so different from plastics, they qualify for different applications than plastics. While plastics prevail in food packaging, this is not a major application for silicone elastomers. Instead, their main application is for repeated use articles either in the household or in professional food processing.

Due to the stability towards environmental influences e.g. temperature, light, humidity etc. lifetime is very high and the articles can be frequently used for many years. Total consumer exposure to potentially migrating substances is low because of the decline of migration over the number of uses and the fact that despite the popularity of certain silicone household articles the proportion in the whole portfolio is quite low. In addition, the standard

assumption applied in food packaging which is 6 dm² contacting 1 kg food is not realistic for the type of articles silicone elastomers are used for. In most cases the surface to volume ratio is lower resulting also in lower migration into food.

Due to their lipophilic features, Silicone elastomers take up non-polar substances. This leads to swelling to a certain extent with organic solvents. In case of contact with vegetable oils, components from these maybe absorbed and penetrate into the elastomer network. This makes simulant D2 and its substitutes, iso-octane and 95% ethanol inappropriate for migration testing on silicone elastomers as they change the physical properties and lead to an overestimation of migration. In several studies it could be shown that simulant D2 and its substitutes iso-octane and 95% ethanol do not reflect migration compared to real food like bake ware or fatty deserts like crème brûlée. Migration into these types of food was clearly below the limit of 10 mg/dm² or 60 mg/kg. For aqueous food simulants (A, B, C and D1), the methods under Regulation (EU) N°10/2011 are appropriate for kitchen articles like baking molds.

4. Test Procedures

One of the basic elements of compliance assessment is the proper selection of substances. For this purpose, it must be ensured that all components comply with any binding texts from the EU Member States, which deals with silicone resins/elastomers intended to be used in contact with food. In this prospect, the following are examples of existing documents that are frequently referred to:

- French Arrêté du 25 Novembre 1992[1]

- German BfR Recommendation XV[2]

The substances used must be of suitable purity. Specifications or use limits as laid down in relevant legal texts have to be respected.

4.1 Silicone Elastomers

4.1.1 Determination of volatile substances

The most important criteria for the determination of compliance of silicone elastomers for food contact with current legislation is the limit for volatile substances of 0.5% as mandatory according to Recommendation XV. Silicones of the BfR and the French Decree of November 25, 1992. Hence, prior to any migration test, determination of volatiles has to be carried out according to the method as laid down in EN 1400-3 (see also the 61st communication of the BfR[3] in Bundesgesundheitsblatt 2003, 46, 362-365).

4.1.2 Migration testing

Prior to migration testing of silicone food contact articles care must be taken that these are clean and dry. Dust may be removed by wiping with a lint-free cloth or brushing it with a soft brush. If according to the use instructions, the article has to be washed prior to its first use, this procedure should be followed as well before the test. The specimens have to be dried over $CaCl_2$ in a desiccator for 48 h at room temperature. The pre-conditioned specimen can then be submitted to migration testing.

MPPO also well known as Tenax is a highly absorptive, porous polymer which was authorized according to Directive 97/48/EC as a solid matrix to substitute fat simulant D at use temperature of 100°C and above. This simulant is authorized under Regulation (EU) 10/2011 (now simulant E) as stand-alone only for articles coming into contact with dried or solid foodstuffs. For other foodstuffs which are frequently prepared using silicone molds or baking mats like pastry, biscuits, cake and bread (food category 02.05 and 02.06) or confectionary products in solid or paste form (food category 03.02), testing with simulant D2 is mandatory according to the before mentioned Regulation. However, as mentioned above, this Regulation does not apply to silicone elastomers and therefore, a separate test regime had to be developed anyway. Comparative tests with different simulants and real foodstuffs demonstrated that for silicone elastomers Tenax is sufficiently conservative to mimic migration into foodstuffs in a pasty or liquid state but becoming solid during the cooking or baking process even in case of cake with high fat content or fatty deserts like crème brulée[5,6]. Hence, due to the inappropriateness of simulant D2 and its liquid substitutes, Tenax is the only alternative for testing migration from silicone elastomer food contact articles into food types covered under category 02.05 and 02.06 or category 03.02.

This is in line with a recommendation of the BfR in previous meetings of the Plastics Commission in 2007 for testing of Silicone Food Contact Articles[4].

The detailed test procedure is laid down in DIN-EN 1186-13 Part B.

5. Evaluation of test results

As the surface to volume ratio of silicone elastomer articles intended to come into contact with food may deviate considerably from the cubic model in packaging applications, it may be inappropriate to express overall migration only in mg/dm². While for packaging applications the cubic model applying a 6:1 ratio for the surface coming into contact with 1 kg food, this is not necessarily realistic for the articles, silicone elastomers are mainly used for. In particular in cases when articles are to be filled like baking molds or which are intended to hold or transport food like baking trays or conveyor belts the cubic model is no longer practicable as the surface to be contacted is considerably lower than in packaging applications. The expression of the overall migration in mg/dm² could implicate a too high level of migration

leading to an unjustified deselection of these materials. For this reason, overall migration should be expressed in mg/kg food. For other articles with unknown surface to volume ratio but for which it can be reasonably expected that the surface to volume ratio is pretty low e.g. closures or dosing valves, overall migration should be expressed in mg/article with 60 mg as the upper limit. For repeated use articles the result of the 3rd migration period has to be taken into account for compliance check. However, if the limit is not exceeded in the 1st test, no further test is necessary. The dedicated fat reduction factors for certain food types should be applied.

6. References

[1]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.

[2]BfR Recommendations on Food Contact Materials XV. Silicones

[3]Bundesgesundheitsblatt 2003, 46, 362-365

[4]122. Sitzung der Kunststoffkommission des BfR, Report of November 29, 2007

[5] Determination of the Overall Migration from Silicone Baking Molds into simulants and Food Using [1]H-NMR Techniques; T.J. Simat et al. ,Food Additives and Contaminants, 2009, 26(3), 395 - 407

[6] Migration behaviour of silicone molds in contact with different foodstuffs, T.J. Simat *et al.*, Food Additives and Contaminants, 2010, 27(3), 396-405