



Collaboration

Prospective study of fatty overall migration of plastic lunch boxes

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Abstract

Overall migration testing is one of the tests performed on plastic materials to prove their compliance with the regulation on plastic materials intended to come into contact with food, Regulation (EU) No 10/2011. Overall migration enables the compliance of the inertia of the material to be verified, such that it does not alter the composition of the food in contact.

Plastic lunch boxes or food containers are a type of article the use of which by the consumers has increased in recent years due to lifestyle, in particular the use of plastic lunch boxes. These articles are nearly always reusable, enabling both the storage and transport of foodstuffs and, in many instances, the heating of food.

The purpose of this work was to provide data regarding the compliance of plastic lunch boxes in relation to fatty overall migration (FOM), applying the methodology outlined in UNE-EN 1186 Standard, under accreditation in the laboratory. The choice of the fatty food simulant for the tests, vegetable oil (simulant D2), was based on the fact that these plastic articles are usually made from polyolefins, materials of apolar character, and for this reason it is reasonable assume that contact with fatty foods would give the worst result in terms of potential migration. To our knowledge, there is no available data published in Spain concerning this type of testing and articles.

Fifteen samples of plastic lunch boxes (for repeated use), of 13 different brands acquired in the retail sector of the Community of Madrid, were analysed for overall migration using vegetable oil (test OM 2). The overall migration limit of 10 mg/dm², in the third migration test, was not exceeded in any of the samples. In 9 out of the 15 samples, quantifiable results were obtained, with values ranging from 1.7 mg/dm² to 6.1 mg/dm².

In addition, with the aim of carrying out a comparison of the results with the conventional D2 simulant and alternative simulants, 11 of the 15 samples were also tested with isooctane (2 days,

20 °C). Only in one of the 11 samples a significant difference between the results was detected, being the value obtained with simulant D2 higher than with isooctane. The mean result of the samples analysed with both simulants (11 samples) was very similar: 3.0 mg/dm² with simulant D2 and 2.1 mg/dm² with isooctane.

Key words

Overall migration, fatty food simulant, plastic packaging.

1. Introduction

Plastic lunch boxes or food containers are a type of article the use of which, due to consumer lifestyle, has increased in recent years because they enable the storage, transport and heating of foodstuffs.

All materials intended for food contact use are regulated at European level by the framework regulation (EU) No 1935/2004 (EU, 2004) on materials and articles intended to come into contact with food. This regulation sets out in article 3 that the materials must not transfer their constituents to foodstuffs in quantities which could endanger human health or bring about an unacceptable change in the composition of the food or bring about a deterioration in the organoleptic characteristics thereof. The requirement prohibiting the alteration of food composition is a demand on the material's inertia for its suitability to come into contact with foodstuffs, limiting the total quantity of substances which could be transferred from the material to the food. In the case of plastic materials, for which a specific European regulation has been established: Regulation (EU) No 10/2011 (EU, 2011), overall migration testing demonstrates the inertia of a material, whereby the migration limit is 10 mg/dm² for articles in general, and 60 mg/kg for articles intended for infants and small children.

Regulation (EU) No 10/2011 defines the overall migration limit as the maximum permitted amount of non-volatile substances released from a material or article into food simulants. Food simulants are test media simulating food; in its behaviour, a simulant mimics migration from the material into the foodstuff. The selection of one simulant over another is based on the type of foodstuff with which it will come into contact. For example, when contact with fatty foods or with foods with fat on the surface is likely, the conventional simulant is the so-called simulant D2, which is any vegetable oil containing less than 1 % unsaponifiable matter (Regulation (EU) 2016/1416 (EU, 2016)).

Plastic lunch boxes tend to be manufactured using polyolefins, apolar polymers; for this reason it is reasonable to assume that contact with fatty foodstuffs would give the worst result in terms of potential migration. Therefore, it was decided that simulant D2 would be used in this study to verify compliance with the overall migration limit. The plastics regulation also foresees the possibility of carrying out screening tests, equal or stricter than those tests using conventional simulants. In these cases substitute simulants, such as isooctane or a 95 % ethanol solution (v/v), are used. Migration tests using substitute simulants are significantly less laborious and complex; however, it must be taken into account that the use of substitute simulants as an alternative to simulant D2 allows to verify compliance, but does not verify non-compliance.

Overall migration testing of plastic materials and articles using conventional simulants is carried out under standardized conditions of time and temperature, taking into account the worst foreseeable conditions in real use. For the testing of samples, the overall migration test OM 2 was chosen (10 days at 40 °C), which would cover prolonged storage at ambient or lower temperature, including the packaging under hot-fill conditions and/or the heating up to a temperature T where $70\text{ °C} \leq T \leq 100\text{ °C}$ during a maximum $t = 120/2 \wedge [(T-70)/10]$ minutes (EU, 2016). For example, this test would cover heating to 70 °C for a maximum of 2 hours, or heating to 100 °C for a maximum

of 15 minutes, conditions which can be experimented when heating of foods in a microwave. Furthermore, since the samples in this study are repeated use articles, the provisions of Regulation (EU) No 10/2011 were taken into account for this type of articles. Therefore, three migration tests are required and the result of the third test is compared with the overall migration limit.

The aim of this study has been to provide data regarding the compliance of plastic lunch boxes in relation to fatty overall migration, applying the methodology outlined in UNE-EN 1186 Standard, and accredited in the laboratory. To our knowledge, there is no available data published in Spain concerning this type of testing and articles. In addition, with the aim of carrying out a comparison of results between the conventional simulant D2 and substitute simulants, some of the samples were also tested with isooctane.

2. Materials and method

2.1 Samples

A total of 15 plastic lunch boxes (repeated use articles), covering 13 different brands, acquired in retail outlets in the community of Madrid were analysed. Sampling was accomplished between June 2015 and November 2016 and 10 of the samples came from the European Union, of which 8 were manufactured in Spain and 2 in Portugal, and 5 samples were of asian origin. The volume of the articles ranged from 100 mL to 1.7 L. According to the labelling, 14 out of the 15 samples were made of polypropylene and one of polystyrene; the identification of the material was confirmed by infrared spectrometry (ATR FT-IR) in the laboratory.

Since the samples were articles intended for repeated use, and taking into account the provisions of Regulation (EU) No 10/2011, it is necessary to perform three migration tests on the same sample, being the result of the third migration test the one which is compared against the overall migration limit. Furthermore, in line with UNE-EN 1186 Standard, the overall migration test using simulant D2 is carried out four times, for which reason it is necessary to test a total of 12 replicated samples to estimate overall migration. In short, determining overall migration using simulant D2 in 15 samples has required to perform 180 migration tests.

In the case of testing using the substitute simulant, isooctane, three replicated tests are required, being nine the total number of migration tests for a repeated use article. Out of the 15 samples acquired, 11 were tested with isooctane (99 migration tests), as well as with simulant D2. To be able to carry out all the tests, for most of the samples 16 units were bought.

The distribution of the tests performed on the samples are shown in table 1.

Types of test	Simulant	No. of samples	No. of tests
Tests by article filling	D2	7	84
	Isooctane	8	72
Tests by immersion	D2	8	96
	Isooctane	3	27

2.2 Reagents and equipment

In line with Regulation (EU) No 10/2011 (EU, 2011) and its amendment Regulation (EU) 2016/416 (EU, 2016), in order to perform the overall migration tests, the conventional simulant D2, a vegetable oil containing less than 1 % unsaponifiable matter, was used. A virgin olive oil mixed with rectified olive oil, acquired in a local store, was used in this study.

Pentane, purity > 98 % (Scharlab), was used as solvent to extract the oil absorbed by the plastic. Glycerol triheptadecanoate (Sigma), was the internal standard in a 2.0 mg/mL solution in cyclohexane (Merck) to quantify the fat absorbed by the plastic. N-heptane, purity > 99 % (Sigma) and derivatizing reagents for the esterification of fatty acids: potassium hydroxide solution (p.a.) (Scharlab) in methanol at 11.0 g/L concentration, boron trifluoride complex (Aldrich) in methanol, 150 g/L and saturated aqueous solution of sodium sulphate (Scharlab), type III water quality or superior.

Isooctane, purity > 99.5 % (Scharlab), was used as the substitute simulant.

An analytical balance with 0.1 mg resolution (Mettler-Toledo) was used for gravimetric determinations. Prior to testing using oil (UNE-EN 1186), the conditioning and checking of the samples was performed in a vacuum oven (Memmert) capable of reaching a temperature of 60 °C ± 5 °C and a pressure ≤13 mb. Migration tests were performed in thermostated ovens (Binder and Memmert), which were also used to dry the capsules in the tests with isooctane. Temperature monitoring during the migration tests was carried out using a calibrated Data Logger with two probes (Ebro). The system used to extract the oil absorbed by the material was a Soxhlet extractor with a bank of heating mantles. The evaporation of the extracts was performed in a rotary evaporator with a water bath at 40 °C under vacuum (Heidolf), and then concentrated to dryness in a sample concentrator (Hypervap), at 35 °C with nitrogen at a flow of 10 bar. Derivatization was carried out in a 70 °C water bath, connected to a serpentine refrigerator in order to obtain the n-heptane reflux. In the tests using isooctane, a vitro-ceramic hot plate (Selecta) was used to evaporate the simulant.

Chromatographic analysis was performed in an Agilent Technologies gas chromatography system connected to a flame ionization detector (6890 series) (GC-FID). The column used was 50 % cyanopropyl-dimethylpolysiloxane, 0.25 µm, 60 m x 0.250 mm (Agilent Technologies DB-23). Helium as carrier gas at a flow rate of 2 mL/min. Oven temperature at 140 °C for 1 minute, followed by an increase at 5 °C/min until reaching 190 °C, holding the final temperature for 8 minutes. The injection volume was 2 µL, in splitting mode with a ratio of 40:1 and 220 °C temperature, 20 mL gas saver. Flame ionization detector at 240 °C, 35 mL/min hydrogen flow, 400 mL/min air flow, 25 mL/min nitrogen flow (Make-up).

2.3 Methodology

Migration tests were performed following internal accredited procedures, based on the UNE-EN 1186 Standard, parts 1, 2, 8 and 14.

Overall migration test using simulant D2 is a gravimetric determination of the material's loss of mass, following the contact with the simulant. In the case of testing with isooctane, a volatile

simulant, the test is a gravimetric determination of the mass of material transferred to the simulant. Therefore, in both cases the tests are based on a gravimetric determination; however, the test using oil is more laborious. Following contact with the material, the use of vegetable oil as a fat simulant makes it necessary to extract and quantify the absorbed oil in order to correct the final mass of the material. Extraction was performed with pentane in Soxhlet and the extract was subsequently derivatized to form methyl esters from the fatty acids, which were quantified by GC/FID. Quantification was performed against calibration curves prepared with 0, 15, 30, 50, 75 and 100 mg of oil, used as the simulant and submitted to the same time and temperature conditions and subsequent derivatization as the samples. Glycerol triheptadecanoate was used as the internal standard.

In migration tests with isooctane, the residual mass was determined following the evaporation of the simulant that came into contact with the samples. This mass is corrected subtracting the residue from the simulant ("blank").

A schematic diagram of the procedures is shown in figure 1.

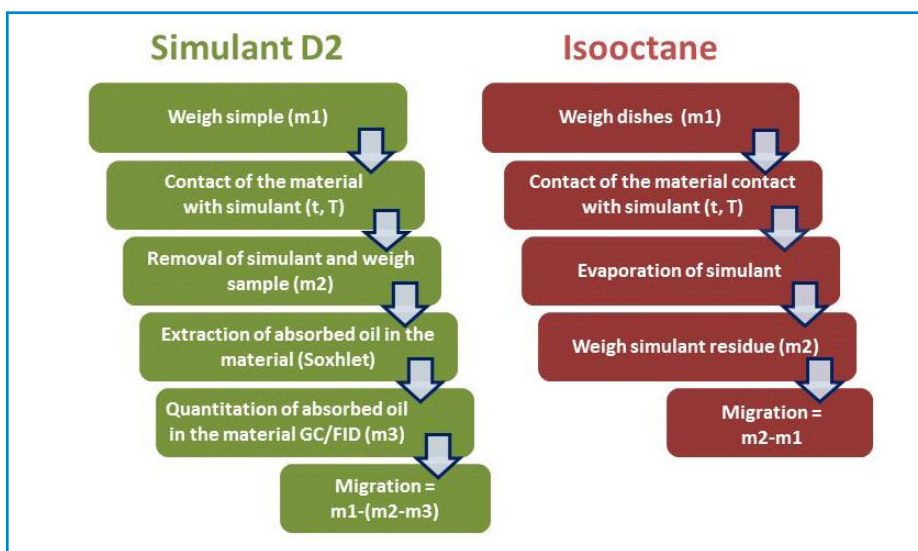


Figure 1. Steps in overall migration testing using simulant D2 and using isooctane.

Testing conditions with simulant D2 were: 10 days at 40 °C (OM 2 test, Regulation (EU) No 10/2011) and for the tests using isooctane, 2 days at 20 °C.

The contact of the samples with the simulant was carried out either by the article filling method (UNE-EN 1186-8) or by the total immersion method (UNE-EN 1186-2) (Table 1). Testing by total immersion was undertaken specifically when testing large volume containers, because the volume of the simulant required for the test by article filling was very large, particularly taking into account the number of replicates necessary to be tested by sample. Since these articles

are monolayer, made up of only one material, it is possible to carry out testing using the total immersion method.

In the total immersion tests, 1 dm² of the sample is exposed to 100 mL of the simulant. If the area of the rims is $\geq 10\%$ of the measured area of the sample, it is included in the calculation of the surface area to estimate the overall migration. In this study, only in one sample it was necessary to take into account the rim area.

In article filling tests, the lunch boxes were filled with the simulant up to 0.5 mm below the rim. The surface exposed to the simulant in testing using the article filling method was calculated in order to subsequently estimate the overall migration in mg/dm².

With regard to the three successive migrations, since the articles were for repeated use, the procedure varied when testing using isooctane and simulant D2. In the first instance, the same sample (in triplicate) was submitted to three successive migration tests, using a new portion of the simulant in each test. In the tests using oil this is not technically possible due to the fact that the material is submitted to an extraction process of the absorbed oil, following the material-oil contact phase. In this case, three groups of replicates of the samples are submitted to three different time periods, which correspond to one, two and three times the test time. For the test conditions employed in this study, four replicates lunch boxes were submitted to 10 days (M1), four replicates to 20 days (M2) and four to 30 days (M3), at 40 °C in all instances. The difference between the results obtained from the samples submitted to 30 days and those tested for 20 days (M3-M2), correspond to the value of the third migration (EU, 2016).

Compliance is verified against the basis of the third migration which should be less than or the same as the migration limit. Furthermore, it must follow that the result of the third migration is not higher the first and the second migration. $(M3-M2) \leq M1$ and $\leq (M2-M1)$.

In order to accept the results as valid, in line with the procedures described in UNE-EN 1186 Standard, in the overall migration test with isooctane, the results of the three replicates must not differ by more than 2 mg/dm², with respect to the mean value. When testing with simulant D2, the tolerance is 3 mg/dm² for values ≤ 10 mg/dm², or 30 % for values > 10 mg/dm², such as that at least three of the replicated results must comply with this tolerance (one result out of the four can be excluded).

3. Results and discussion

A total of 15 samples of plastic lunch boxes were tested for overall fat migration, which represented a total of 180 migration tests using vegetable oil. Of the 15 samples, 11 were additionally tested using the substitute simulant isooctane (99 tests).

Quantifiable results were obtained (limit of quantification= 1 mg/dm²) in 9 samples using simulant D2, with values ranging from 1.7 mg/dm² to 6.1 mg/dm², and in 6 samples using isooctane, ranging between 1.3 mg/dm² and 3.4 mg/dm². The individual results obtained are shown in figure 2 and a summary of these in table 2.

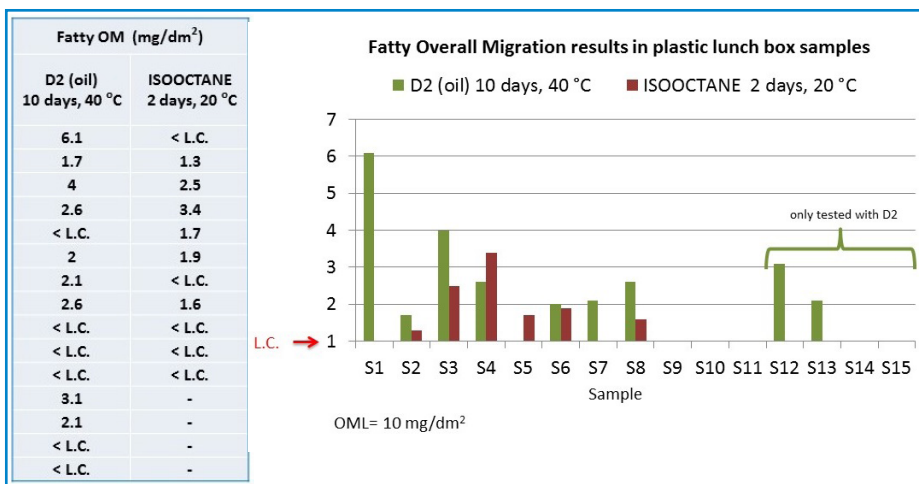


Figure 2. Fatty overall migration results of lunch boxes samples.

Table 2. Summary of tests and results of overall migration in samples of lunch boxes		
Simulant	Test by article filling	Test by immersion
Simulant D2	7 samples 100 %> LOQ Mean value= 2.6 mg/dm ²	8 samples 2> LOQ Mean value= 4.1 mg/dm ²
Overall (n=9 samples > LOQ)	2.9 mg/dm ²	
Isooctane	8 samples 4> LOQ Mean value= 2.2 mg/dm ²	3 samples 2> LOQ Mean value= 1.8 mg/dm ²
Global (n=6 samples > LOQ)	2.1 mg/dm ²	

For the comparison of the results obtained using the conventional simulant D2 (10 days at 40 °C), and using the substitute simulant, isooctane (2 days at 20 °C), the uncertainty associated with both testing procedures must be taken into account. The uncertainty (estimated in the laboratory) for simulant D2 is $U(k=2) = \pm 3.0 \text{ mg/dm}^2$, and for isooctane, $U(k=2) = \pm 1.3 \text{ mg/dm}^2$. Considering these uncertainties, it can be said that only in one sample the results obtained differed with both simulants (D2> isooctane). On the other hand, if the mean quantifiable values of the analysed samples are compared with both simulants (11 samples, Figure 2), the mean value obtained using simulant D2 (3.0 mg/dm²) does not differ significantly from the mean value of the samples using isooctane, 2.1 mg/dm².

All the samples of lunch boxes analysed for fatty overall migration (15) were compliant with the limit of 10 mg/dm², established in the regulation of plastic materials/objects that come into contact with foodstuffs (EU, 2011). In relation to the requirement provisioning that there must not be an

increase in three successive migrations, it must be pointed out that only in one sample (6.1 mg/dm²) it was not the case, because though there was not a significant increase from the second to the third migration, an increase relating to the first migration was detected. This sample was made of polystyrene, unlike the rest of the samples which were made from polypropylene. The testing of this sample using isooctane gave unquantifiable results in all three migration tests.

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