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OVERALL MIGRATION ASPECTS FOR PLASTIC FOOD CONTACT MATERIALS WITH FOOD SIMULANTS USING SPSS STATISTICS

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Abstract

Food can come into contact with several materials and articles before being consumed during production, processing, storage, preparation and serving. Plastic is the most widely used packaging material globally. Overall migration represents the total amount of non-volatile substances that can migrate from a food packaging material into food. It can be determined gravimetrically by exposing the item to a food simulant for a specified and appropriate length of time. The aim of the research was to evaluate the overall migration phenomenon for several food contact materials according to the conditions specified in Regulation (EU) no. 10/2011 [6].

Simulants A (10% ethanol), B (3% acetic acid), C (10% ethanol), D1 (ethanol 50%) and D2 (olive oil) were used to quantify overall migration from the following plastic food contact materials: polyethylene terephthalate (PET), polypropylene (PP), high-density polyethylene (HDPE), medium-density polyethylene (MDPE) and low-density polyethylene (LDPE) using 4 different testing conditions: OM1 (10 days at 20 ^{0}C), OM2 (10 days at 40 ^{0}C), OM3 (2 hours at 70 ^{0}C) and OM4 (1 hour at 100 ^{0}C). Migration testing is represented by the measurement of the overall migration by a gravimetric determination of all chemical substances that migrate to the simulant. SR EN 1186-2003 standards were used for the analysis of overall migration (parts 1, 2, 3, 7 and 9). Interpretation and analysis of the data was made using SPSS Statistics Data Editor Program. The variability was determined with ANOVA method.

The overall migration studies using food simulants mentioned above shows that the migration rate was very low, far below the allowed limit (10 mg/dm^2). ANOVA one-way analysis indicates significant differences between the means for average migration related to product type, simulants and extraction conditions ($\sigma < 0.05$). At high temperature the overall migration is increasing. The same is when the extraction time is higher.

The overall migration limit is a measure for the inertness of the material. All tested materials can be used as food packaging materials given that conditions used for testing cover most of the conditions used in practice.

***Key words**: Overall migration, Plastic, FCM, simulants, SPSS.*

1. Introduction

Food Contact Materials (FCMs) is the generic term for all type of materials and articles that come into contact with food during its production, preparation and serving, before its eventual consumption. Food contact materials are either intended to be brought into contact with food, are already in contact with food, or can reasonably be brought into contact with food or transfer their constituents to the food under normal or foreseeable use [1].

According to EU Regulation 1935/2004, [2], on materials and articles intended to come into contact with food, there are 17 types of materials and articles that can be used in contact with food. Of these, plastics are the most common and most wide-ranging materials used for food packaging. The volume of plastic allocated to food packaging represents around 40% of total plastics [3]. Global plastic demand is dominated by polypropylene (PP), polyethylene (PE), and polyvinyl chloride (PVC), followed by polystyrene (PS), and polyethylene terephthalate (PET) [4].

Migration is defined as the phenomenon that occurs when chemical substances present in a polymer migrate to the surface of the polymer item or to a medium in contact with the polymer. Migration of chemical substances from plastic food contact materials is generally undesired, since some of the migrating

substances can be toxic. Overall migration testing from plastic materials using food simulants consists in two steps. First step is represented by the exposure of the plastic to the food simulant(s) according to appropriate conditions (time, temperature and simulant). The second step of migration testing is represented by the measurement of the overall migration by a gravimetric determination of all chemical substances that migrate to the simulant [5]. The overall migration limit (OML) is the maximum permitted total amount of non-volatile substances that can migrate from a food contact material into food. EU Regulation 10/2011 on plastic materials and articles, [6], has set out an OML value of 10 mg/dm^2.

This study aim was to evaluate the overall migration of components into food simulants from different types of common food plastic contact materials, and to find correlations between migration and factors that can influence the migration phenomenon using ANOVA statistical method.

2. Materials and Methods

For the study several common plastic food contact materials were used: polyethylene terephthalate (PET), polypropylene (PP), high-density polyethylene (HDPE), medium-density polyethylene (MDPE), and low-density polyethylene (LDPE). The materials were provided by different Romanian producers.

Tests were conducted according to EU Regulation 10/2011, [6], and the SR EN 1186:2003 standard, parts 1, 2, 3, 7, and 9 [7 - 11], using the following simulants: 10% ethylic alcohol (Simulant A), 3% acetic acid (Simulant B), 20% ethylic alcohol (Simulant C), 50% ethylic alcohol (Simulant D1), and olive oil (Simulant D2). Four different extraction conditions were used: OM1 (10 days at 20 ^{0}C), OM2 (10 days at 40 ^{0}C), OM3 (2 hours at 70 ^{0}C) and OM4 (1 hour at 100 ^{0}C) (Figure 1).

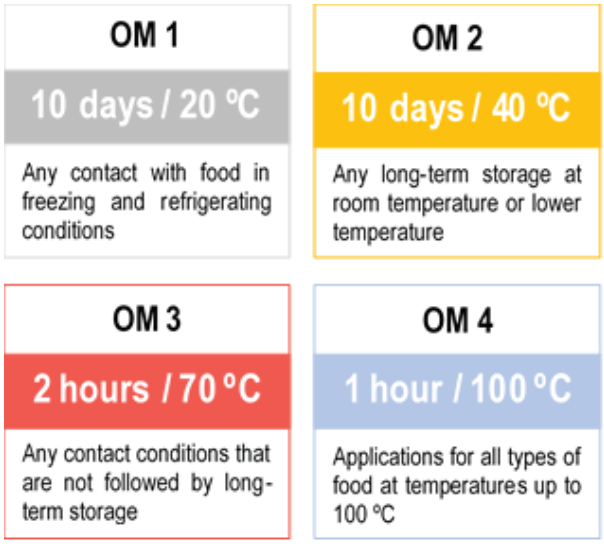

Figure 1. Testing conditions for overall migration according to EU Regulation 10/2011 [6]

The food simulants are used as substitutes for food due to chemical analysis simplification. They vary in terms of their chemical properties, thus representing several particular food types: hydrophilic (water-based), lipophilic (fatty foods) or amphiphilic (foods with both watery and fatty properties). Butter and other amphiphilic foods are for example simulated by a 50% ethanol in water solution. For oily foods, vegetable oil is the prescribed food simulant, whereas simulants 10% ethanol or 3% acetic acid in water have to be applied for water-based foods and drinks (Table 1).

Table 1. Food simulants (according to EU Regulation 10/2011 [6])

Simulant	Food type
A - 10% ethylic alcohol	Aqueous Food
B - 3% acetic acid	Foods that have a hydrophilic character and are able to extract hydrophilic substances and which have a pH below 4.5
C - 20% ethylic alcohol	Foods that have hydrophilic character and are able to extract hydrophilic substances, alcoholic foods with alcohol content of up to 20 % and foods containing a relevant amount of organic ingredients that render the food more lipophilic
D1 - 50% ethylic alcohol	Alcoholic foods with an alcohol content of above 20% and dairy products
D2 - olive oil	Fatty food and foods which contain free fats at the surface

Data analysis considered possible correlations between average migration and different factors, like material type, simulant used or extraction conditions. Interpretation and analysis of the data was made using SPSS Statistics Data Editor Program. The variability was determined with ANOVA method. Testing scheme is outlined in the test matrix shown in Table 2.

Table 2. Test matrix

Material	Product	Simulant					Extraction conditions			
		A	B	C	D1	D2	OM 1	OM 2	OM 3	OM4
PET	PET 200	✓	✓	✓	✓	✓	✓	✓	✓	✓
	PET 250	✓	✓	✓	✓	✓	✓	✓	✓	✓
	PET 300	✓	✓	✓	✓	✓	✓	✓	✓	✓
	PET 500	✓	✓	✓	✓	✓	✓	✓	✓	✓
	Tray	✓	✓	✓	✓	✓	⊘	✓	✓	✓
	Bottle	✓	✓	✓	✓	✓	⊘	✓	✓	✓
	Preform	✓	✓	✓	✓	⊘	⊘	✓	✓	✓
PE	HDPE film	✓	✓	✓	✓	✓	✓	✓	✓	✓
	MDPE film	✓	✓	✓	✓	✓	✓	✓	✓	✓
	LDPE film	✓	✓	✓	✓	✓	✓	✓	✓	✓
PP	PP film	✓	✓	✓	✓	✓	✓	✓	✓	✓

Legend: OM 1 - Overall migration 10 days at 20 ^{0}C; OM 2 - Overall migration 10 days at 40 ^{0}C; OM 3 - Overall migration 2 hours at 70 ^{0}C; OM 4 - Overall migration 1 hour at 100 ^{0}C.

3. Results and Discussion

To study the overall migration, the materials presented in Table 1 were analysed according to the conditions stated in EU Regulation 10/2011. The results are presented as mean of three results and standard deviation was calculated. Obtained data are listed in Tables 3 - 6.

ANOVA one-way analysis indicates significant differences between the means for average migration related to product type, simulants and extraction conditions ($\sigma < 0.05$).

Table 3. Overall migration results after extraction 1 hour at 100 ^{0}C

Sample	Overall migration (OM) - 1 hour at 100 ^{0}C									
	OM in Sim. A (mg/dm^2)		OM in Sim. B (mg/dm^2)		OM in Sim. C (mg/dm^2)		OM in Sim. D1 (mg/dm^2)		OM in Sim. D2 (mg/dm^2)	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
PET 200	0.17	0.000	0.42	0.000	0.20	0.046	1.17	0.000	1.30	0.173
PET 250	0.22	0.046	0.47	0.046	0.31	0.098	1.22	0.046	1.30	0.100
PET 300	0.25	0.000	0.50	0.000	0.53	0.128	1.28	0.046	1.40	0.100
PET 400	0.30	0.046	0.56	0.098	0.61	0.052	1.53	0.046	1.40	0.000
PET 450	0.36	0.052	0.67	0.000	0.70	0.046	1.64	0.052	1.50	0.200
PET 500	0.42	0.000	0.72	0.046	0.92	0.165	1.72	0.046	1.60	0.173
PET tray	0.66	0.085	0.83	0.085	1.17	0.085	1.25	0.080	1.0	0.137
PET preform	1.19	0.127	1.03	0.128	1.33	0.085	2.08	0.165	n. a	n. a
PET bottle	0.89	0.052	1.0	0.080	1.17	0.085	1.67	0.085	1.40	0.083
HDPE film	0.95	0.046	1.28	0.046	1.47	0.092	1.80	0.046	0.84	0.057
PP film	1.22	0.046	1.19	0.046	1.42	0.085	2.03	0.046	0.88	0.056
LDPE film	1.0	0.080	1.33	0.085	1.44	0.046	2.08	0.085	0.95	0.050
MDPE film	0.53	0.046	0.53	0.046	1.50	0.080	2.0	0.080	1.30	0.030

Table 4. Overall migration results after extraction 2 hours at 70 °C

Sample	Overall migration (OM) - 2 hours at 70 °C									
	OM in Sim. A (mg/dm²)		OM in Sim. B (mg/dm²)		OM in Sim. C (mg/dm²)		OM in Sim. D1 (mg/dm²)		OM in Sim. D2 (mg/dm²)	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
PET 200	0.47	0.092	0.17	0.000	0.22	0.046	0.58	0.085	0.90	0.044
PET 250	0.47	0.046	0.22	0.046	0.45	0.046	0.81	0.098	1.0	0.131
PET 300	0.59	0.144	0.33	0.085	0.50	0.000	0.92	0.661	1.10	0.056
PET 400	0.64	0.052	0.42	0.000	0.55	0.046	1.11	0.242	1.10	0.142
PET 450	0.67	0.000	0.47	0.046	0.64	0.052	1.22	0.046	1.30	0.060
PET 500	0.72	0.046	0.53	0.128	0.67	0.000	1.53	0.046	1.50	0.080
PET tray	0.66	0.085	1.0	0.144	0.83	0.085	0.83	0.085	1.22	0.119
PET preform	1.17	0.085	1.0	0.080	1.17	0.085	1.89	0.052	n. a	n. a
PET bottle	0.77	0.046	0.86	0.052	1.08	0.128	1.47	0.092	0.70	0.056
HDPE film	0.36	0.052	0.64	0.052	1.02	0.046	1.92	0.085	1.02	0.070
PP film	0.64	0.052	0.50	0.080	1.0	0.080	2.30	0.046	1.20	0.046
LDPE film	0.50	0.080	1.47	0.046	0.97	0.046	2.05	0.046	1.17	0.044
MDPE film	0.53	0.046	1.28	0.046	1.05	0.046	1.45	0.046	1.35	0.050

Table 5. Overall migration results after extraction 10 days at 40 °C

Sample	Overall migration (OM) - 10 days at 40 °C									
	OM in Sim. A (mg/dm2)		OM in Sim. B (mg/dm2)		OM in Sim. C (mg/dm2)		OM in Sim. D1 (mg/dm2)		OM in Sim. D2 (mg/dm2)	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
PET 200	0.33	0.085	0.75	0.144	0.7	0.046	1.45	0.046	1.30	0.026
PET 250	0.33	0.085	0.78	0.128	0.81	0.098	1.58	0.144	1.60	0.062
PET 300	0.36	0.052	0.72	0.046	0.84	0.144	1.86	0.128	1.70	0.035
PET 400	0.36	0.098	0.84	0.144	1.0	0.144	1.95	0.046	1.80	0.070
PET 450	0.36	0.098	0.86	0.098	0.97	0.092	2.08	0.217	1.90	0.072
PET 500	0.39	0.052	0.86	0.172	1.06	0.127	2.19	0.237	1.90	0.060
PET tray	0.83	0.085	0.94	0.127	1.33	0.160	1.73	0.101	1.70	0.072
PET preform	1.14	0.052	1.33	0.085	1.77	0.146	2.69	0.098	n. a	n. a
PET bottle	1.0	0.080	1.19	0.046	1.25	0.080	1.83	0.085	1.30	0.053
HDPE film	0.50	0.080	0.89	0.052	1.02	0.012	1.72	0.046	0.86	0.038
PP film	0.50	0.000	0.80	0.046	0.86	0.052	1.64	0.052	1.03	0.030
LDPE film	0.47	0.092	1.14	0.052	0.7	0.035	1.78	0.046	1.17	0.020
MDPE film	0.58	0.085	0.83	0.085	1.03	0.046	1.45	0.046	1.20	0.085

Table 6. Overall migration results after extraction 10 days at 20 °C

Sample	Overall migration (OM) - 10 days at 20 °C									
	OM in Sim. A (mg/dm2)		OM in Sim. B (mg/dm2)		OM in Sim. C (mg/dm2)		OM in Sim. D1 (mg/dm2)		OM in Sim. D2 (mg/dm2)	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
PET 200	0.20	0.046	0.39	0.052	0.14	0.052	1.41	0.144	1.20	0.079
PET 250	0.22	0.046	0.47	0.046	0.39	0.098	1.50	0.144	1.30	0.056
PET 300	0.28	0.046	0.47	0.046	0.39	0.052	2.28	0.128	1.40	0.053
PET 400	0.44	0.127	0.47	0.046	0.42	0.144	2.36	0.098	1.40	0.070
PET 450	0.53	0.092	0.50	0.000	0.45	0.046	2.47	0.046	1.60	0.090
PET 500	0.61	0.052	0.56	0.098	0.53	0.128	2.61	0.098	1.80	0.061
HDPE film	0.77	0.046	0.67	0.085	0.92	0.085	2.08	0.085	0.64	0.052
PP film	0.45	0.046	0.70	0.046	0.75	0.080	1.42	0.085	0.98	0.046
LDPE film	0.55	0.046	1.58	0.085	0.80	0.046	2.14	0.052	0.85	0.052
MDPE film	0.50	0.080	0.72	0.046	0.83	0.085	1.25	0.080	1.20	0.066

Average migration related to product (Figure 2) shows dependencies between migration values and thickness, in the case of PET films. Also, very close values were obtained for PET preform and bottle, as well as for PP and PE (HDPE, MDPE, and LDPE).

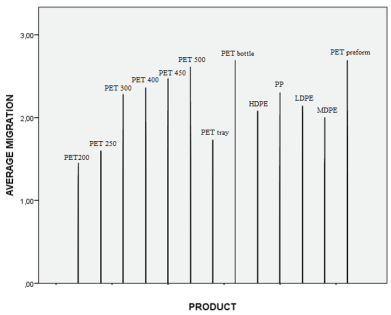

Figure 2. Sum of average migration by product

Average migration related to simulant (Figure 3) shows significant differences, especially between aqueous simulants (A, B and C) and fatty simulants (D1 and D2). Simulant D2 (50% ethylic alcohol) is the most "severe" simulant while simulant A (10% ethylic alcohol) is the "gentlest".

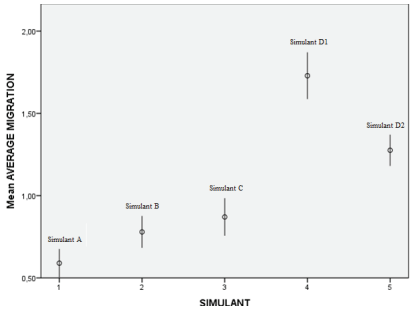

Figure 3. Sum of average migration by simulant type

Average migration related to extraction conditions (Figure 4) shows significant differences between time and temperature. At high temperature (OM4 - 100 Celsius degrees) the overall migration is increasing. The same is when the extraction time is higher (OM2 - 10 days). This is way, when checking for the compliance of food contact materials with overall migration limit is important to choose the most appropriate conditions intended for use (Figure 1).

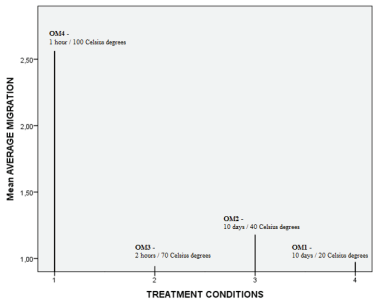

Figure 4. Sum of average migration by extraction conditions

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4. Conclusions

- Overall migration study was conducted on 3 different types of commonly used food contact materials. Four different extraction conditions were used and the test were performed using aqueous and fatty simulants.

- ANOVA analysis was used to highlight possible correlations between average migration and different factors, such as simulant, extraction conditions and type of material. The results indicate significant differences between the means for average migration related to factors mentioned above ($\sigma < 0.05$).

- The values obtained for overall migration, in all food simulants used, were well below the limit of 10 mg/dm2, specified by EU Regulation 10/2011, which means that all tested products are safe to be used in contact with food.

5. References

[1] EFSA Panel on Food Contact Materials, Enzymes, Flavourings and Processing Aids - (CEF). (2016). *Recent developments in the risk assessment of chemicals in food and their potential impact on the safety assessment of substances used in food contact materials*. EFSA Journal, 14, 1, pp. 4357.

[2] European Parliament and Council (2004). Regulation (EC) no 1935/2004 on materials and articles intended to come into contact with food and repealing Directives 80/590/EEC and 89/109/EEC. OJ., L 338.

[3] Mohanty F. and Swain S. K. (2017). *Bionanocomposites for Food Packaging Applications*. In: Grumezescu A., Oprea A. (Eds.), Nanotechnology Applications in Food, Elsevier, Netherlands, pp. 363-379.

[4] Hahladakis J. N, Velis C. A., Weber R., Iacovidou E., Purnell P. (2018). *An overview of chemical additives present in plastics: Migration, release, fate and environmental impact during their use, disposal and recycling*. Journal of Hazardous Materials, 344, pp. 179-199.

[5] Bradley E. L., Castle L., Jickells S. M., Mountfort K. A., Read W. A. (2009). *Use of overall migration methodology to test for food-contact substances with specific migration limits*. Food Additives & Contaminants: Part A, 26, 4, pp., 574-582.

[6] EU Commission. (2011). *Regulation (EU) no 10/2011 of on plastic materials and articles intended to come into contact with food*. OJ., L 12.

[7] SR EN 1186-1:2003. (2003). *Materials and articles in contact with foodstuffs - Plastics, Part 1: Guide to the selection of conditions and test methods for overall migration*.

[8] SR EN 1186-2:2003. (2003). *Materials and articles in contact with foodstuffs - Plastics, Part 2: Test methods for overall migration into olive oil by total immersion*.

[9] SR EN 1186-3:2003. (2003). *Materials and articles in contact with foodstuffs - Plastics, Part 3: Test methods for overall migration into aqueous food simulants by total immersion*.

[10] SR EN 1186-7:2003. (2003). *Materials and articles in contact with foodstuffs - Plastics, Part 7: Test methods for overall migration into aqueous food simulants using a pouch*.

[11] SR EN 1186-9:2003. (2003). *Materials and articles in contact with foodstuffs - Plastics, Part 9: Test methods for overall migration into aqueous food simulants by article filling*.