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MODEL STUDY ON INTENSIFIED MIGRATION OF VOLATILE SUBSTANCES FROM FOOD CONTACTING PLASTIC MATERIALS DURING REPEATED MICROWAVING

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ABSTRACT

This model experiment was aimed towards determination of the effect of repeated microwaving on migration of volatile substances to food simulating model solutions from packages commonly used in food industry. For this purpose 5 most common plastic packages were selected: white round shaped polypropylene container for ready to eat courses, its polystyrene cover, yellow polypropylene cup of 175 cm^3 capacity, white polystyrene cup of 135 cm^3 capacity and polystyrene/polyethylene foil; 3% acetic acid, 15% ethanol and rectified olive oil were taken as food simulating solvents. Prior to microwaving, the samples were stored for 10 days in 5°C. Using the GC/MS combined with static head space technique, 26 substances migrating into food simulants were identified after storage and prior to microwave heating. Cumulative exposure time to microwaving ranged from 2 till 30 min. It was found that repeated microwaving increased by 400% global migration of volatile substances from yellow polypropylene cup into olive oil. Above 50% increase was found for olive oil in other packages. Also, in polystyrene cup two fold increase of global migration into 15% ethanol was observed. Therefore plastic packages intended for single use and not designed for microwaving should not be used for repeated heating of foods in microwave ovens.

Key words: migration, food packages, microwaving

INTRODUCTION

Microwave radiation may increase the rate of physicochemical processes, including the migration of plastic package components into food product [5]. Most of these components belong to group of foreign substances and contaminate food product because of toxic and/or mutagenic effect [9]. The number of chemicals that could be used for manufacturing of packaging plastics exceeds 2000 [2]. It has also been demonstrated that microwave processing of food may result in intensified migration of package components, e.g. cyclic and aliphatic hydrocarbons, benzene, benzaldehyde, BHT and other [6]. However, due to technological progress in packaging industry within past several years, the global migration of foreign substances from packagings into food decreased by more than thirty-fold [8].

Plastic food packaging materials are assumed to be disposable ones. In the reality however, and under the conditions of household, the attractive packages are frequently re-used several times, particularly for mild heating in microwave ovens. Therefore this experiment was aimed towards determination of the effect of repeated microwaving on migration of volatile substances to food simulating model solutions from packages commonly used in food industry.

MATERIALS AND METHODS

The experiment was performed with five most common commercial materials used for packaging of food products and these were: white round shaped polypropylene container for ready to eat courses (M1), its polystyrene cover (M2), yellow polypropylene cup of 175 cm^3 capacity (M3), white polystyrene cup of 135 cm^3 capacity (M4) and polystyrene/polyethylene foil (M5).

Pieces 5 x 5mm of the material were placed into sealed vials of 7 cm^3, and 4 cm^3 of food simulant solution was added. The simulation of package - food contact during storage prior to microwaving was carried out under the circumstances of European Commission Directive 93/8/EEC [3], and contact time was 10 days in temperature of 5°C. Three food simulant solutions were used in the experiment: 3% (w/v) acetic acid, 15% (v/v) ethanol and rectified olive oil, as recommended in the Directive 93/8/EEC (1985).

After 10-day storage, the samples were microwaved. Output power of the oven was 540 W, and it was determined according to ASTM F-1317-90 [1]. For each combination of package/solution, 9 microwaving duration spans, ranging from 4 to 30 min, were applied. To avoid overheathing of the seals, single exposure took 30 s followed with intensive cooling of vials in iced water. Number of these cycles was depending on cumulative exposure time required.

An analysis of samples (static headspace technique) was conducted with capillary gas chromatograph / mass spectrometer SATURN II GC/MS (Varian):

- column: Stabilwax (Restek), 30 m length, 0.25 mm Id,
- oven temperature: 70°C - 5 min., to 120°C - 5°C/min., 120°C - 5 min,
- injector temperature: 180°C,
- detector temperature: 180°C,
- carrier gas: helium,
- flow rate: 33 cm/s

Identification of migrating substances was based on mass spectra and NIST92 Mass Spectra Library. For determination of global migration, styrene and ethylbenzene were taken as the standards.

RESULTS AND DISCUSSION

At least 26 substances were found and identified in food simulating solutions prior to microwaving (Table 1). This was a consequence of 10 days long direct contact of the solution with the package. Nonanal appeared to be the most frequent substance found in all analysed systems of food simulant/package. Next in the order of frequency were heptane, octanal and hexenal. These results are in good agreement with the data of Linssen [7].

Table 1. Substances identified prior to microwaving in food simulating solutions after 10 days storage at 5°C (M1 – white polypropylene, M2 – colourless polystyrene cover, M3 – yellow polypropylene, M4 - white polystyrene, M5 - polystyrene/polyethylene foil)

No	Substance identified	Food simulating solution												No of cases
		3% acetic acid		15% ethanol					Rectified olive oil					
		M3	M4	M1	M2	M3	M4	M5	M1	M2	M3	M4	M5	
1	dimethylhexane							◆						1
2	buthanol												◆	1
3	cyclohexane			◆										1
4	cycloheptatriene	◆						◆	◆	◆			◆	5
5	decane			◆	◆	◆								3
6	diethoxyethane			◆	◆	◆	◆	◆						5
7	dimethylcyclopentane	◆	◆											2
8	ethylbenzene			◆	◆		◆						◆	4
9	hexane			◆	◆								◆	3
10	hexenal		◆			◆			◆	◆	◆	◆	◆	7
11	heptane	◆	◆	◆	◆	◆	◆			◆	◆	◆		9
12	heptanal	◆	◆			◆					◆	◆	◆	6
13	heptenal		◆											1
14	hexanoic acid	◆	◆											2
15	xylene												◆	1
16	acetic acid			◆	◆	◆	◆			◆				5
17	methylethylbenzene												◆	1
18	nonane			◆	◆									2
19	nonanal	◆	◆	◆	◆	◆	◆	◆	◆	◆	◆	◆	◆	12
20	ethyl acetate							◆						1
21	octanal		◆			◆	◆	◆	◆	◆	◆		◆	8
22	pentanal												◆	1
23	propylbenzene												◆	1
24	styrene		◆	◆	◆		◆						◆	5
25	carbon tetrachloride												◆	1
26	toluene			◆	◆	◆	◆							4
Number of substances identified		6	9	11	10	9	8	6	4	6	5	4	14	

Table 2 summarises qualitative data obtained in the experiment. This is evident, that number of migrated substances depends on type of the pacakge as well as food simulant.

The highest risk of migration of foreign substances from plastic packages into food during regular storage occured for low alcohol and aqueous food, since in 15% ethanol 44 cases of migration were confirmed (regardless the package type). Second in the order of risk was the olive oil, i.e. fatty food. In 3% solution of acetic acid that stands for acid foods, probability of migration was much lower.

Table 2. Number of identified substances in particular packaging materials/model solution system prior to microwaving

Packaging material	3% acetic acid	15% ethanol	Olive oil	Total number of cases
Polypropylene container, white (M1)	-----	11	4	15
Polystyrene container cover, colourless (M2)	-----	10	6	16
Polypropylene cup, yellow (M3)	6	9	5	20
Polystyrene cup, white (M4)	9	8	4	21
Polystyrene/polyetylene foil white (M5)	-----	6	14	20
Total number of cases	15	44	33	

Table 3. Migration reference values for styrene and ethylbenzene (mg/dm^2; average of package types ± standard deviation)

Substance	Food simulating solution		
	15% ethanol	3% acetic acid	olive oil
Styrene	5.08±2.2	21.6±9.5	81.1±33.3
Ethylbenzene	11.25±9.20	nd*	79.8±30.8

*nd – not determined.

The risk associated with migration depends also on type of package used. For polystyrene/polyethylene foil and commercial cups total number of positive cases was 20 – 21 and was higher by, at least 25%, in comparison with polypropylene container (M1) and it's cover (M2).

Frequently the migration patterns do not follow the Fickan models. For this reason the effect of microwaving on migration was calculated with reference to the values of global migration determined in the controls and not exposed to microwave radiation (Table 3).

Relative migration expresses the ratio of actual migration level to the values obtained just after storage = 100%. This enables distinct description of influence of microwaving time with reference to the end of storage, i.e. in relative figures. The curves of relative migration of volatile substances as function of cumulative microwaving time are shown in Figures 1- 5.

Fig. 1. Relative global migration values from white polypropylene container into food simulating solvents (M1) as a function of microwaving time

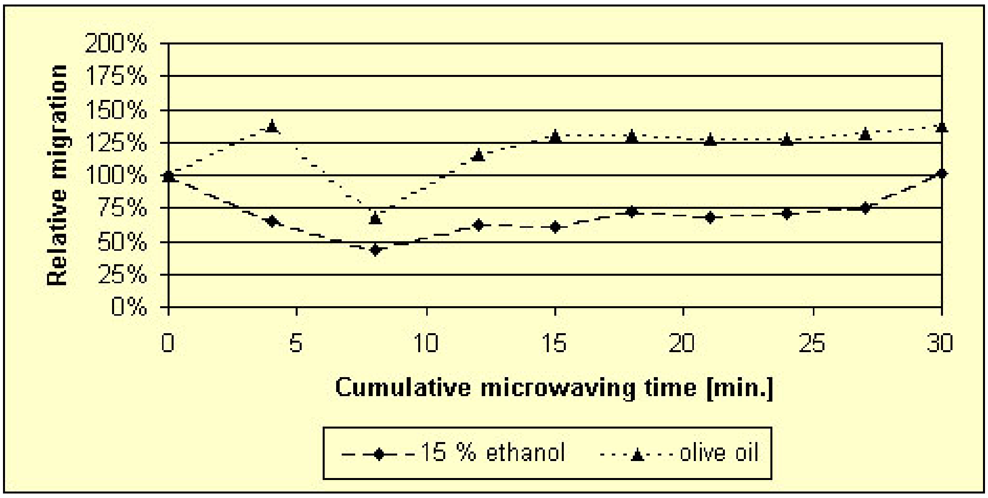


Fig. 2. Relative global migration values from polystyrene cover (M2) of polypropylene container (M1) into food simulating solvent as a function of microwaving time

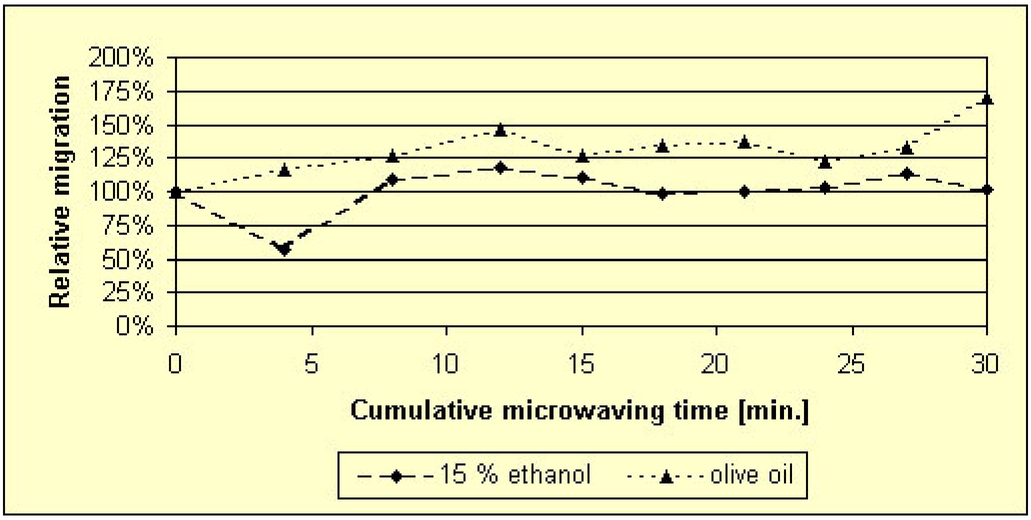


Fig. 3. Relative global migration values from yellow polypropylene cup (M3) into food simulating solvents as a function of microwaving time

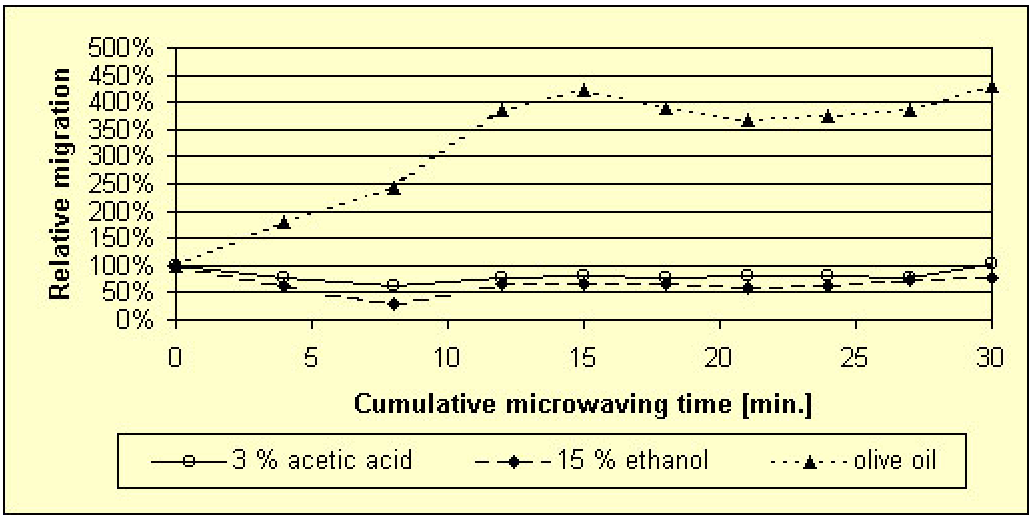


Fig. 4. Relative global migration values from white polystyrene cup (M4) into food simulating solvents as a function of microwaving time

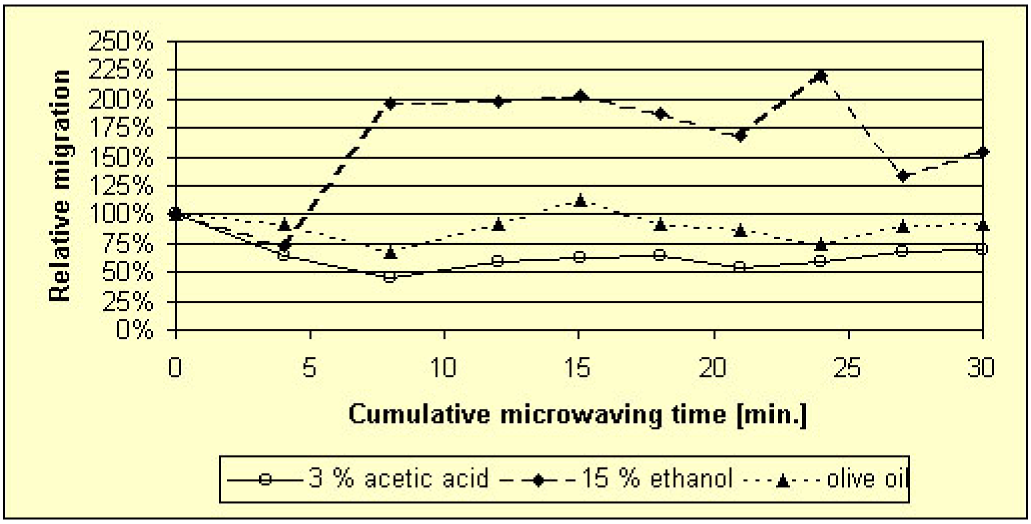
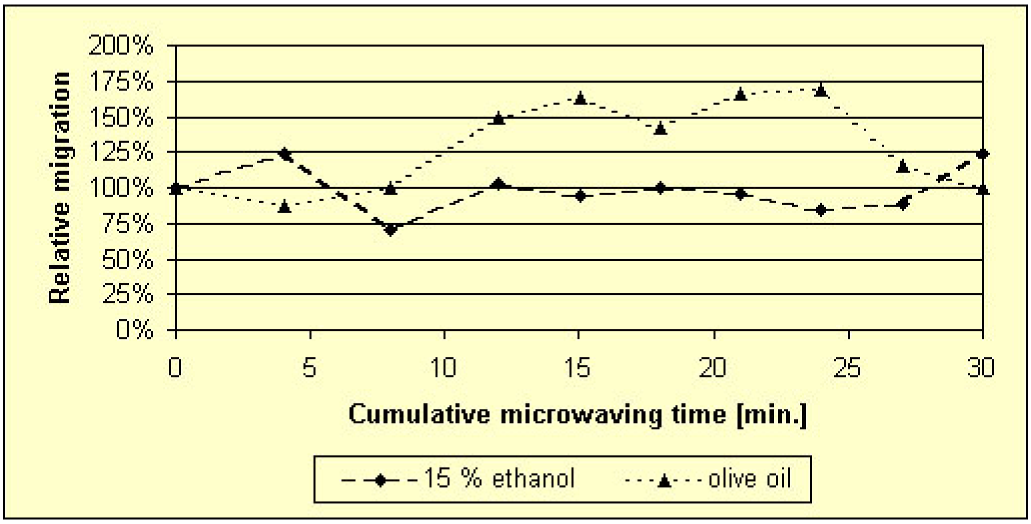


Fig.5. Relative global migration values form polystyrene/polyethylene foil (M5) into food simulating solvents as a function of microwaving time



The most drastic rise of global migration was observed in yellow polypropylene cups (Fig. 3), as cumulative exposure time extended 12 min. Relative value of global migration in olive oil reached level of about 400% in comparison with not treated samples. Next in the order of migration intensity was polystyrene cup, from which global migration to 15% ethanol was doubled after 8 min of cumulative exposure.

Fatty foods when microwaved, were also sensitive to absorption of volatile substances from the packages. After 12 min of cumulative exposure global migration to olive oil increased by above 50% in the PS/PE foil, white polypropylene container and it's colourless polystyrene cover.

Data in Figures 1-5 deliver also another important information. Pathway of the curves indicates, that short-time single exposure to microwaves does not substantially increase the risk of intensified migration of volatile substances from plastic packages into food. However, as soon as cumulative exposure time exceeds sensitive region of 4-8 min, the amount of foreign substances migrating into food might be increased. Therefore plastic packages intended for single use and not designed for microwaving should not be utilised for multiple warming in an oven. Thus the problem whether proper information such as "do not use for microwaving" should appear on the package label, is worth a consideration.

CONCLUSIONS

The use of commercial plastic packages for repeated microwaving is associated with the risk of increased migration of volatile substances into food. This effect becomes distinct as soon as cumulative exposure time to microwaves exceeds 4-8 min at 540 W output power. Intensity of migration phenomena depends on type of package and on food simulating solvent. The highest 400% increase in global migration after repeated microwaving was found for olive oil in yellow polypropylene cups. Plastic packages intended for single use and not designed for microwaving should not be used for repeated heating of foods in microwave ovens.

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