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The Effect of Microwave on Migration of Styrene Monomer Polystyrene Food Packaging and Compared to other Thermal Processes

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ABSTRACT: The migration of packaging material constituents into food is a product of the interaction between the food and packaging material. This phenomenon is of importance because some migrating substances may be toxicologically carcinogenic and endanger the consumer safety. Polystyrenes are used in many food-contact applications for the packaging of aqueous-based, fatty and dry foods. The correlation of residual styrene concentrations in polystyrene with styrene migration into food-simulating solvents is of interest in order to predict the potential exposure of consumers to styrene from food-packaging applications. GC-Mass chromatography was used to determine the migration of styrene monomer into food simulant. Differential simulants (water, 10% ethanol, 3% acetic acid and olive oil) were used to evaluate the effect of heat treatments on styrene migration. It was observed that the migration of styrene is significantly higher in microwave and traditional thermal process than vacuum heating. In additions among different simulants, ethanol had significant higher migration than other simulants. Migration of styrene was increased after 30 minutes heating in all treatments. In addition, the amount of polystyrene migration into the simulants was below the standard limit set by the European Commission for secure PS food packaging.

Keywords: *Migration, Polystyrene, Simultant, Styrene Monomer.*

Introduction

Styrene monomer (C_6H_5-CH=CH_2), used in polystyrene plastic packaging can migrate from the container to food under environmental conditions such as temperature and then enter the body. When styrene monomer vapors enter the human body, they have significant impacts on body such as skin irritation, irritation to the eyes, nose, and throat and the symptoms mainly appear quickly. The chronic effects of styrene monomer are related to its metabolites, styrene oxide in particular, that has destructive effects on the central nervous system and liver. Toxic effects of styrene monomer on the reproductive system, respiratory, nervous system, **digestive system**, lymph nodes and other organs have been studied by researchers and research centers in recent decades therefore the results of these studies indicate that the body is vulnerable to styrene monomer specially in the respiratory and digestive system. To control the amount of migration of various compounds from packaging materials to the food, the European Union have established and imposed rules and restrictions (Beldi *et al*., 2012). Baner *et al*. (1992) observed that

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increasing the temperature can increase the migration. Twafik *et al*. (1998) reported that styrene migration depends on the food stimulant.

Because of the convenience and high-speed heating of microwave for domestic use, the use of this technology has been increased considerably in recent years. In this regard, food manufacturers have tried to produce containers suitable for heating food in the microwave oven. Polystyrene containers which are processed by microwave are the most widely used containers for food packaging. Therefore, in this research it has been attempted to examine the amount of migration of styrene from polystyrene containers to different food environments while they are being processed in the microwave oven.

Materials and Methods

-Samples

Clear plastic disposable cups (200 cc) known as GPPS plastic containers were bought randomly from wholesale centers in the market.

-Preparation of containers and heating conditions

Cuts of 5×5 mm of GPPS plastic were prepared from packaging material and weighed with an accuracy of 0.0001 g and placed in a container of 22 ml of food stimulants. The container was closed with Teflon tape and a metal cap to prevent the evaporation of material during testing. Samples of different food stimulants in polystyrene containers were kept for 5 days in the refrigerator (4 °C) and then subjected to various thermal processes (DIN EN1186-3, 2002).

- To process by microwave, a domestic microwave oven with a frequency of 4.2 GHz and 900 watts was used. Each of the prepared samples was heated in it for 30 minutes.
- In order to process by conventional heating, the food environments were put in the in polystyrene containers and then placed in a hot air oven with a temperature of 80 °C for 30 minutes.
- To heat in the vacuum, the food environments were put in the polystyrene containers and then placed in the vacuum oven for 30 minutes.

-Stimulant

Due to the complexity of the physical structure of food, the general testing of migration are performed by using food stimulants to understand the migration more clearly. According to European Union and Iranian Standard Organization, stimulants consisted of groups; a: water as an aqueous environment stimulant, b: 3% acetic acid as an acidic food stimulant, c: 10% ethanol as an alcoholic food stimulant, d: refined olive oil as a fatty food stimulant (Organization INS. Plastics).

-Determination of styrene

The standard solutions and extracts were analyzed with a gas chromatography-mass spectrometry using a ShimadzuGC14A QP-1100 EX MS detector (Kyoto, Japan) equipped with a SPB-5 capillary column (30mlong×0.25mmi.d. with 0.5µmfilm thickness) (Supelco, Bellefonte, PA, USA). Helium was employed as the carrier gas, with a head pressure of 153 KPa. Temperatures for injector and detector were set at 180 °C and the column oven was programmed initially at 70 °C for 5 min, then heated with a constant rate of 10 °C/min to a final temperature of 280 °C that was held for 5 min. Samples (2µl) were injected in the splitless mode (1.5 min splitless period).

-Determination of Diffusion coefficient and Activation energy

Arrhenius type equation is the equation correlating diffusion coefficient and temperature (Bastarrachea *et al.*, 2010):
Equation (1)

$$D_P = D_0 e^{-\frac{E}{RT}}$$

D_0 = pre-exponential factor, E = activation energy for diffusive molecules, R = gas constant, and T = absolute temperature of the system. Several approaches have been carried out to develop a new model for predicting diffusion of compounds, where $D_p = f$ (molecular mass of migrant, absolute temperature). Brandsch *et al*. (2000) developed this correlation:

Equation (2)

$$D_P = D_0 \exp\left(A_p - 0.1351 M_r^{2/3} + 0.003\ M_r - \frac{10454}{RT}\right)\ cm^2/s$$

M_r is the relative molecular mass of the migrant

Equation (3)

$$A_P = A_P^{\prime} - \frac{t}{T}$$

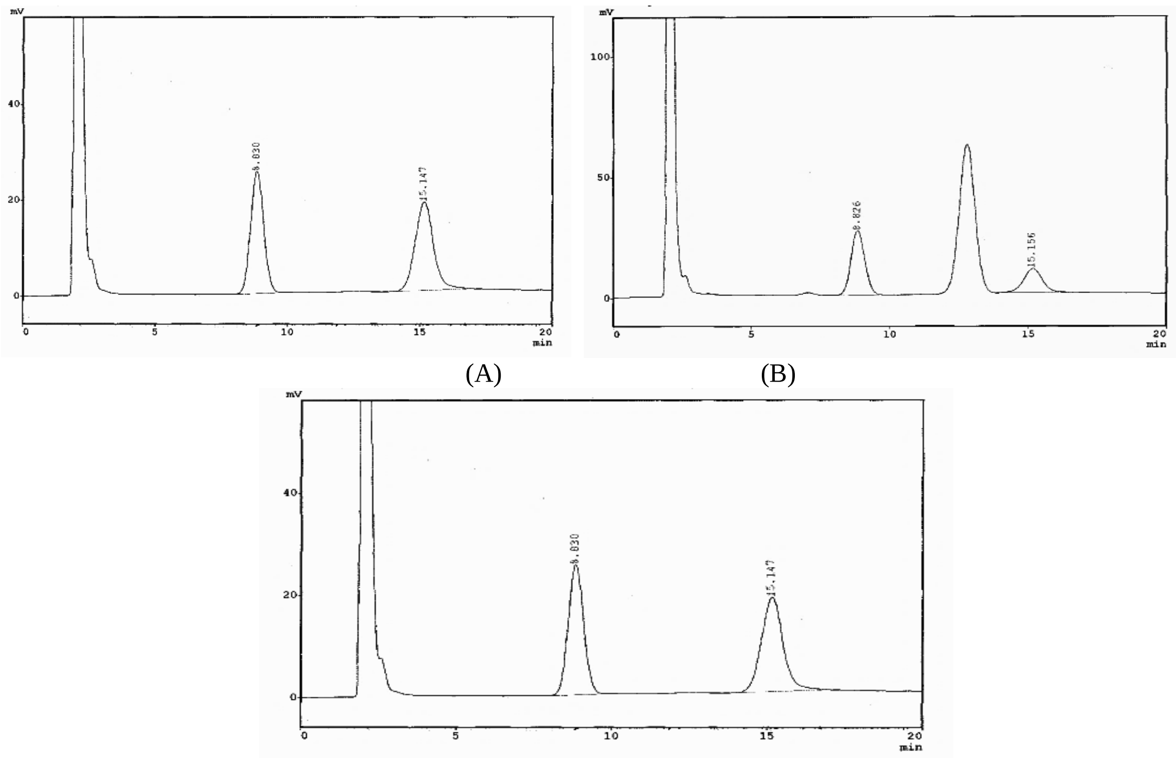
$A_P^{\prime}$ and τ= specific parameters of the polymer matrix.

-Statistical analysis

Analysis of variance (ANOVA) was applied and two-tailed independent-sample T-test in SPSS 19.0 software (SPSS Inc., Chicago, IL, USA) was performed to calculate significant differences among the different treatments. Total experiments were carried out in triplicate orders to approve the statistical significance of all data.

Results and Discussion

Based on the results obtained after the preparation of the standard curve and its evaluation, the correlation coefficient r= 99/0 was observed. The standard curve equation for styrene monomer was y = 1.8 × 10^2X + 2.7 × 10^3. To make the standard curve, concentrations of 0.25, 0.5, 1, and 2.5 ng/ml of styrene monomer were used ten times for ten consecutive days and the results were used to determine the unknown samples.



(C)

Fig. 1. Chromatogram of styrene monomer in different food stimulant samples (A) conventional heating (B) Microwave heating (C) vacuum heating.

Chromatography profile of the derived solution by three heating (conventional heating, microwave heating, and vacuum) treatments is shown in Figure 1. The first peak in the chromatogram represents acetonitrile where the retention time is about 3 minutes and the second peak is related to styrene monomer. The initial concentration of styrene monomer in polystyrene sheets was 520 mg/kg, but its average value in polystyrene dishes was 225 mg/kg which was low compared to the results (Banner *et al*., 2000). In this study, the migration of styrene monomer was observed in all clear disposable cups prepared as laboratory samples.

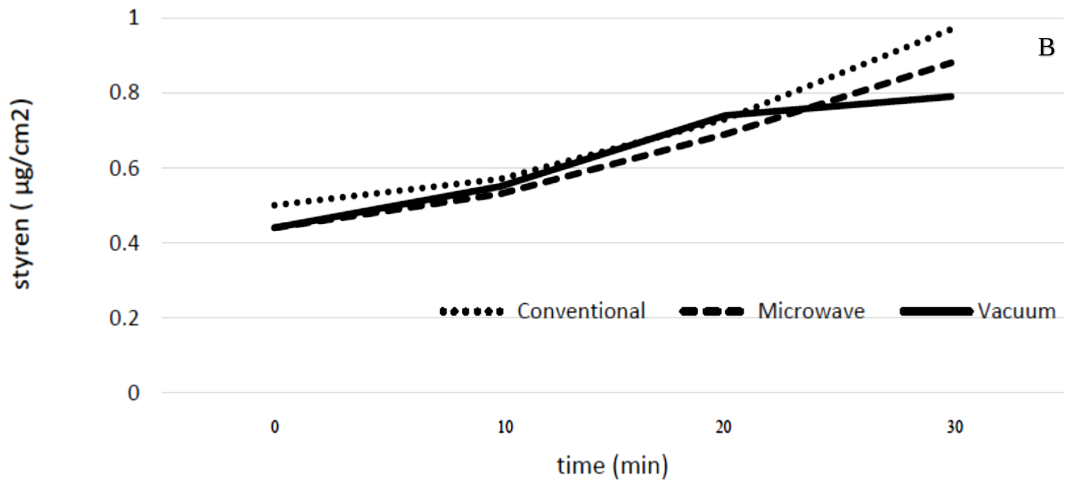


Fig. 2. The amount of migration in food stimulant water by different heating processes.

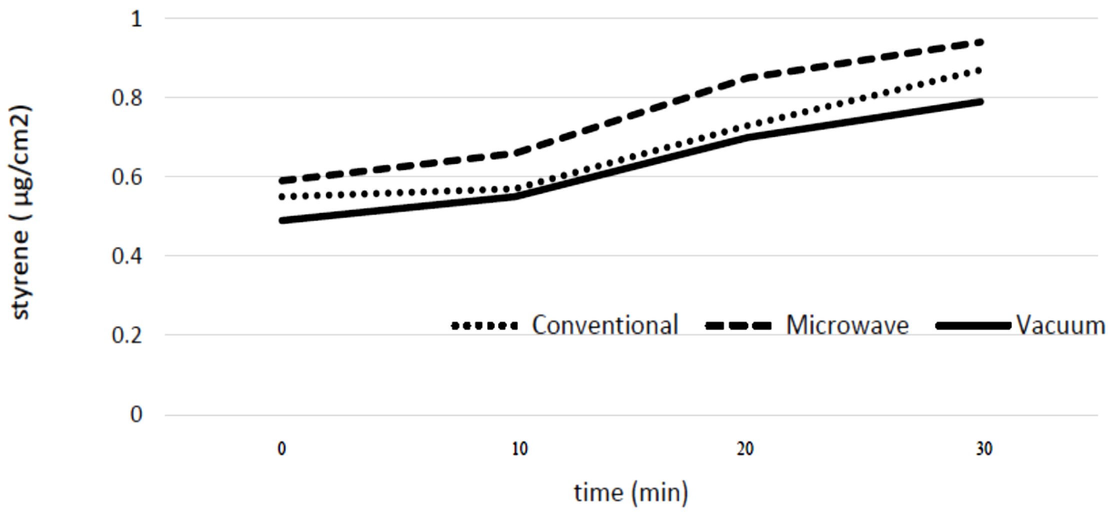


Fig. 3. The amount of migration in food stimulant ethanol %10 by different heating processes.

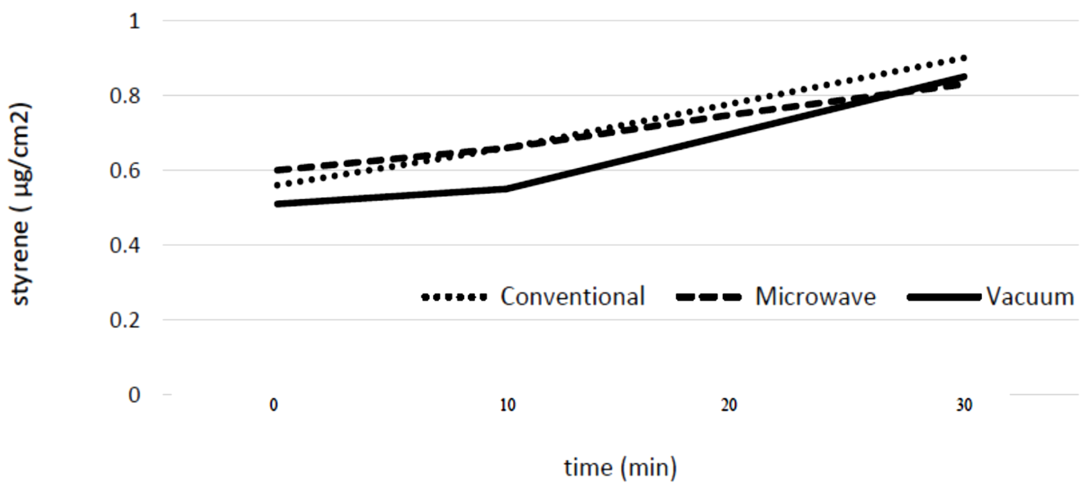


Fig. 4. The amount of migration in food stimulant acetic acid by different heating processes

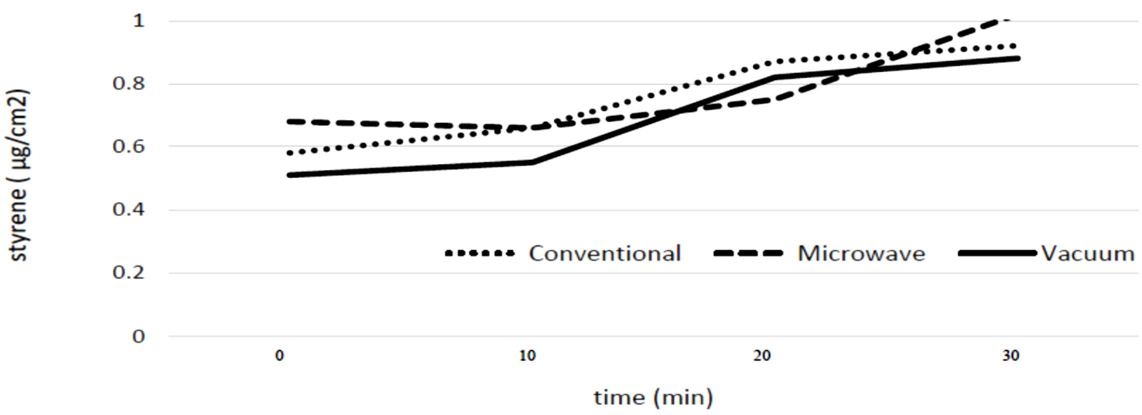


Fig. 5. The amount of migration in food stimulant refined olive oil by different heating processes.

Table 1. Discriptional statistics of variables in different heat treatments in four simulants

Simulants	Heat treatment	0(min)	10(min)	20(min)	30(min)
	Conventional	0.5^{bc}	0.57^{fg}	0.73^{m}	0.97^{v}
water	Microwave	0.44^{a}	0.53^{d}	0.69^{kl}	0.88^{r}
	Vacuum	0.44^{a}	0.55^{e}	0.74^{mn}	0.79^{o}
	Conventional	0.55^{e}	0.57^{fg}	0.73^{m}	0.87^{r}
ethanol 10%	Microwave	0.59^{hi}	0.66^{j}	0.85^{q}	0.94^{u}
	Vacuum	0.49^{b}	0.55^{e}	0.7^{l}	0.79^{o}
	Conventional	0.56^{ef}	0.66^{j}	0.78^{o}	0.9^{s}
acetic acid 3%	Microwave	0.6^{i}	0.66^{j}	0.75^{n}	0.83^{p}
	Vacuum	0.51^{c}	0.55^{e}	0.7^{l}	0.85^{q}
	Conventional	0.58^{gh}	0.66^{j}	0.87^{r}	0.92^{t}
olive oil	Microwave	0.68^{k}	0.66^{j}	0.75^{n}	1.02^{w}
	Vacuum	0.51^{c}	0.55^{e}	0.82^{p}	0.88^{r}

Data are means of triplicate measurements. Values with different superscript upper case letters are statistically significant at $P < 0.05$.

The amount of migrated styrene monomer from dishes to different food stimulants in different heat conditions (Figures 2-5, Table 1) shows that temperature as an important factor could affect the migration of styrene monomer. All samples migrated according to the standard of legal limit of migration of styrene (less than 0.1 mg/cm^2) (national standard of Iran, No. 13737). The migration experiments show that higher temperature will lead to rapid migration at a higher speed; On the other hand, there is a linear relationship between the mass flow per unit area and the square root of time that is consistent with Fick's law of diffusion. By examining the rate of styrene monomer migration of all styrene monomer used in dishes and considering the dishes are between 225 ppm styrene monomer level, the observed migration rate equals to the average % 0.005 of all the styrene monomer used in the container. Microwave can affect the migration of packaging substances in two ways; both through direct effect of microwave and also indirect effect of microwave by increasing temperature as a result of heating food. Microwaves cause water molecules in the food to vibrate, and as the waves are absorbed by the food, they cause its temperature to rise. Considering the molecular vibrations, microwaves could accelerate the migration of substances in food simulants. Because the spin polarization and ionic polarization are the main production mechanisms in relation with microwave heating, water stimulants from water and acid attack can increase migration. However, the migration in ethanol and oil stimulants by microwave compared with conventional heating is low. On the other hand, the non-uniform heating of microwaves compared to the conventional heating and vacuum can increase the migration of compounds. The amount of styrene monomer measured in various food samples such as hot drinks like tea was determined between 7-8 ppb and the temperature has been regarded as the most important factor in migration (Synder *et al*., 1984). Two other reports of two studies carried out by Veraart and Coulier (2007) have been published. In the first report, the amount of migration determined by GC shows that by increasing the temperature from 40 °C to 100 °C, the level of migration increases and reaches to 13-14 ppb, and in the second report, when the amount of migration was measured by HPLC, the same results was observed and the level of temperature increase and food storage time in these dishes were examined and it was revealed that by increasing these two factors simultaneously, the amount of migration goes up to the level of 15 ppb. According to the report, the level of determined styrene monomer in polystyrene dishes in contact with hot drinks specially boiling water at 100˚C in one hour was 7 pbb, and it was 14 pbb in laboratory condition at the same temperature in two hours. According the result of the conducted research, extending the storage time will increase the amount of styrene monomer migration to drinks to the level of 17 pbb. Twaf *et al*. (2008) also observed that styrene migration depends on the food stimulant. Examining the migration of different compounds during heating the polymers, Banner *et al*., (2000) discovered that increasing the temperature in conventional heating can increase the migration significantly. By examining the effect of storage time on styrene migration, it was revealed that thermal process after 30 minute increases migration in all treatments significantly (Figure 2 to 5).

According to Table 2, the values of A_p and τ for styrene monomer infiltration from polymer are 2.2 and 14554 respectively (Piringer & Baner, 2008). The values of diffusion coefficients and activation energy calculated by equation (1) and (2) for different processes are shown in Table 1. The obtained diffusion coefficients were

Table 2. The amount of diffusion coefficient and activation energy in different food stimulants by three heating processes

Heating Method	stimulant	Diffusion coefficient (cm^2/s)	Activation energy (J/g mol.)
Conventional	water	$5.4 \times 10^{-18\ a}$	1447.1^{a}
Conventional	ethanol %10	$6.57 \times 10^{-18\ b}$	1513.4^{b}
Conventional	Acetic Acid	$5.8 \times 10^{-18\ a}$	1477.4^{a}
Conventional	refined olive oil	$5.49 \times 10^{-18\ a}$	1447.7^{a}
Microwave	water	$5.7 \times 10^{-18\ a}$	1467.3^{a}
Microwave	ethanol %10	$6.2 \times 10^{-18\ b}$	1501.4^{b}
Microwave	Acetic Acid	$5.9 \times 10^{-18\ a}$	1486.7^{a}
Microwave	refined olive oil	$5.86 \times 10^{-18\ a}$	1449.3^{a}
Vacuum	water	$5.25 \times 10^{-18\ c}$	1431.1^{c}
Vacuum	ethanol %10	$5.34 \times 10^{-18\ c}$	1439.1^{c}
Vacuum	Acetic Acid	$5.07 \times 10^{-18\ c}$	1412.2^{c}
Vacuum	refined olive oil	$5.19 \times 10^{-18\ c}$	1424.7^{c}

Data are means of triplicate measurements. Values with different superscript upper case letters in a column are statistically significant at $P < 0.05$.

more than those for n-heptane and ethanol in Miltz and Murphy's tests (Choi *et al*., 2005; Miltz *et al*., 2005), Various food stimulants have different diffusion coefficient because of reaction between polymer and food stimulant (Gyasyn *et al*., 2005).

Some fluids as food stimulants influence on mass transfer from certain polymers particularly when the solubility of solvent and polymer are of the same amount. In other words, when non-polar solvents of food stimulant are used with non-polar polymer, great migration occurs. The opposite is also true (Begley *et al*., 2004). 10% ethanol can be used as a polar food stimulant in contact with non-polar polymer (Choi *et al*., 2005). Therefore, the value of diffusion coefficient of ethanol stimulant in all treatments is higher than other stimulants. Pennarun *et al*. (2004) also concluded that ethanol contact increases the diffusion coefficient of migration compounds to an acceptable level, which results from the swelling of amorphous polymer. On the other hand, according to the Piringer equation, diffusion coefficient is totally dependent on temperature; thus, the determined amounts vary in different thermal processes (1994). The amount of diffusion coefficient of microwave and conventional heating is significantly higher than vacuum that is probably due to low reaction between food compounds in vacuum condition. High amount of activation energy in all treatments can be attributed to high molecular weight of migratory component (styrene monomer).

Conclusion

Differential food simulants (water, 10% ethanol, 3% acetic acid and olive oil) were employed to evaluate the effect of heat treatments (Conventional, Microwave and Vacuum) on styrene migration. The data obtained in this study showed that the migration of styrene is significantly lower in vacuum heating than microwave and traditional heating. Furthermore the results confirmed that among different simulants, ethanol had significant higher migration than other simulants and the level of polystyrene migration into the simulants was below the standard limit set by the European Commission for secure PS food packaging.

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