Studies of Migration of Styrene Monomer from Polystyrene Packaging into the Food Simulant

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Abstract

Migration of styrene monomer from polystyrene (PS) dishes was conducted during this research at temperatures of 5, 20, and 40°C. According to the Food and Drug Administration (FDA) regulations, these experiments were performed in contact with 10% ethanol as a food simulant for the oil in water (o/w) emulsions. The dishes were filled in each of the defined temperatures and stored for 35 days. In relatively close intervals (1, 7, 15, 24, and 35 days) the amount of migration which occurred was determined by means of Head Space Gas Chromatography Mass Spectrometry (HS-GC-MS). By increasing storage time and temperature, the amount of migration was increased and in all times and temperatures styrene monomer was detected. In addition, a mathematical model based on the Fick’s second law was validated to predict migration from packaging material into the 10% ethanol. The resulted diffusion coefficients were 3.6×10⁻¹⁸, 4.9×10⁻¹⁸, and 6×10⁻¹⁸ (m²/s) in 5, 20 and 40°C respectively.

Keywords: Migration, Polystyrene, Diffusion Coefficient, HS-GC-MS

1. Introduction

One of the unavoidable factors in food manufacturing is Packaging [1]. Packaging is not only a science, but also an art and the technology of protecting products from the overt and inherent adverse effects of the environment [2]. Nowadays, Plastic packaging is the most common among other packaging materials, because of its relatively cheap price, convenience and outstanding service properties [3]. In food packaging the mass exchange between the environment, package and food is called permeation, migration and sorption [4]. Although these phenomena are important in food packaging, migration could threaten the consumer safety, so scientific and legislative communities have been paid more attention to the amount of migration which is taking place during storage. Styrene is used mainly for the production of polystyrene (PS) and styrene copolymers. It is the second most widely used monomer for production of food-contact packaging polymers [5]. Migration of styrene monomer from PS dishes causes an undesirable flavor and taint

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to the foods [6]. It was reported that serum prolactin level is increased by exposure to a highly concentrated styrene monomer in humans [7]. Styrene has been found to be metabolized to styrene 7, 8 oxides and several in vitro and in vivo studies revealed that this metabolite can be carcinogenic [8]. Mass transfer from plastic material into foodstuffs in most cases obeys Fick’s law of diffusion. Modeling of potential migration is already used by the US Food and Drug Administration (FDA) as an additional tool to assist in making regulatory decisions [9]. On the other hand, migration experiments are used when resulted data are higher than regulatory limitations.

In the migration experiments, food simulants are used to simplify the analytical procedures. Food simulants are selected compounds that produce similar interactions with foods [4]. It means that they should simulate the extent and kinetics of migration, but in particular they only simulate the extent of migration, because in most cases they are fluid [10]. Although there have been several reports on the migration of styrene monomers, dimmers, and trimmers into the heptan and water by Jin Ok Choi et. al, and also other experiments on the migration of styrene monomers into 8% ethanol by Murphy et. al [3, 11], in this study the effect of the hot filling process of the selected simulant on the migration rate of the styrene monomer was investigated because some dairy products like cream cheese were filled hotly, in order to flow more easily in the distributing tubes. Therefore, the present study was done to evaluate the migration behavior of the styrene monomer from PS packaging into 10% ethanol as a food simulant when filled at 65°C and the determination of diffusion coefficient in two different temperatures of 5, 20, and 40°C.

2. Experimental part
2-1. Material and method
The reference material, styrene monomer (CAS 100-42-5) was supplied by Merk Company. Commercially produced PS dishes (100mL) were obtained from PEGAH packaging company. Water (grade number AG0001, volatile materials: 0.0001%) and ethanol were purchased from sigma. In these experiments the materials were purchased, as we wanted to avoid any contamination which may interfere in the GC analysis. In this work 10 mL of the sample was used for GC analyses.

The HS-GC-MASS (Aiglent HP 6890 N Gas Chromatograph Aiglent Technology, PaloAlto, CA) condition for water/ethanol extracts: gas chromatograph-Agilent technologies, the column was HP-5 (5%methylphenyl siloxane) with 30m length, 320µm ID and 100µm film thickness (model 6890) with mass spectrometer detector (model 5973) in SIM mode: quotation ions were: m/z 51, 78, 103, 104, 105, Carrier gas was helium (purity 99.99%), Oven temperature program from 40°C (30 min) to 150°C (12.5°C/min), held for 1min and to 280°C (30°C/min).

Calibration: six aqueous solutions of styrene of known concentration (50-750ppb) were prepared from 100ppm of styrene (10% ethanolic). The above-mentioned standard aqueous solutions were used for preparing the calibration graph.
2-2. Migration tests
Migration tests were conducted by filling PS dishes with food simulant. In all cases, the solvent was added to the dishes and stored for 35 days at selected temperatures. Since cutting polymers for migration tests have been shown in other polymer systems to cause anomalous results when compared with single sided measurements [12], in this study the dishes are in one sided contact with the food simulant and no cutting was done.

Determination of potential migrant in PS dishes
A total 1±0.001g of the sample was cut into small pieces and 25mL of methylene chloride was added. The bottle was then capped tightly and placed in a mechanical shaker until the polymer was completely dissolved (FDA). 3 µL of the resulted solution was injected to the gas chromatograph.

Determination of apparent diffusion coefficient
To assess migration of additives and contaminants from food packaging films, mathematical modeling based on Fick's second law was used. Hence, in addition to the experimental methods, a new alternative tool based on theoretical migration experiments appears to be applicable. In order to solve partial differential equation, Crank (1975) has formulated initial and boundary conditions as flows: 1) the migrant is homogeneously distributed in the polymer matrix, 2) there is no boundary resistance between the polymer and food, 3) there is no swelling due to the absorption of the food, and interactions between the polymer and food is negligible, 4) a partition coefficient between the polymer and food is assumed and defined. With these assumptions, Fick's second diffusion equation has the following analytical solution [13].

\[
\frac{m_{F,0}}{A} = C_{p,0} \rho_p d_p \left(\frac{\alpha}{1+\alpha}\right) \times \left[1 - \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)}{1+\alpha + \alpha^2 q_n^2} \exp\left(\frac{q_n^2 D t}{l^2}\right)\right]
\]

In this equation, \(m_{F,0}\) (mg), are the mass migrates from the P to F, A is the contact area with the polymer, \((\text{cm}^2)\), \(C_0\) is the concentration of the contaminant in the polymer, \((\text{mg/kg})\), \(\rho_p\) is the polymer density, \((\text{g/cm}^3)\), \(d_p\) thickness of the polymer, cm, \(V_L\) and \(V_F\), volume of the F and P, \(D\) is diffusion coefficient, \(q_n\) is the positive roots of equation \(\tan q_n = -\alpha q_n\), and \(K_P/F\) is the partition coefficient of the migrant between P and F.

3. Results and discussion
The gas chromatographic profile of the extract solution obtained by Head Space Gas Chromatography- Mass Spectrometry (HS-GC-MS) is shown in Fig. 1, in which the styrene monomer peak appeared after 8.9 min. The initial concentration of styrene monomer in PS sheets was determined 625 mg/kg, but the average styrene monomer level in PS containers was 224 mg/kg, which, in comparison with the resulted data is low [14].

The migration of styrene monomer from PS was very slow at all temperatures tested. Fig. 2 shows the kinetic plot for the mass transfer of styrene monomer into 10% ethanol at 5, 20, and 40°C. Migration experiments showed that higher temperatures
yielded a faster migration rate and, on the other hand, there is essentially a linear relationship between the mass migration per unit surface area and the square root of time. This is consistent with Fick’s law of diffusion.

![Figure 1](image1.png)

Figure 1. The Gas chromatography profile of styrene monomer in PS sheet.

![Figure 2](image2.png)

Figure 2. Migration of styrene monomer into 10% ethanol at 5, 20, and 40°C from PS dishes.
The resulted experimental data in three different temperatures were fitted to Eq. (1) by non-linear regression, with MATLAB software. From the series of the experimental data on migration level (µg/cm²) versus time, the model parameter $D$ was $3.6 \times 10^{-18}$, $4.9 \times 10^{-18}$, and $6 \times 10^{-18}$ (m²/s) in 5, 20 and 40°C respectively. The resulted diffusion coefficients were much lower than the experimental data reported by Jin Ok Choi and Miltz and Rosen-Doody for n-heptane and cooking oil, respectively ($5 \times 10^{-14}$, $3.49 \times 10^{-12}$ m²/s both at 40°C respectively) [3, 6], but resulted diffusion coefficients to some extent are close to the data reported by Murphy et al. for 8% ethanol, which was $3.6 \times 10^{-18}$ m²/s in 40°C [11]. Fig. 3 shows the experimental migration values and estimated migration curves of the styrene monomer in 5, 20, and 40°C.

Figure 3. Migration of styrene monomers into 10% ethanol from PS packaging at different temperatures a) 5°C b) 25°C c) 40°C. The solid line is the calculated migration according to the equation (1)
Different types of food simulants give different types of diffusion coefficient due to the interactions between the polymer and food stimulant [15]. It has been recognized for many years that certain food simulating liquids will affect the mass transfer from certain polymers [16]. This is especially true when the solubility parameters of the solvent and the polymer are similar in magnitude. In other words, when non-polar food simulating solvents are used with non-polar polymers, excessive migration can occur. The reverse is true [12]. In the current case, 10% ethanol can be considered a polar food simulant in contact with non-polar polymer. Tawfik and Huyghebaert also observed that styrene migration was dependent on food simulant [17]. Banner et al. proposed ethanol as a simulant for fatty foods because it has little interaction with many plastics such as polyolefins, the migrants are readily soluble in it, and it is easy to work with analytically [18]. The US FDA recommends 50% ethanol as a food oil substitute simulant for PS materials [19].

4. Conclusions
In this study, styrene monomer was selected because of the toxicological properties of this monomer and 10% ethanol was selected as a substitute of the O/W emulsions according to the FDA. As expected, the migration was increased by increasing the time and temperature of the experiments. The apparent diffusion coefficient is also calculated in three defined temperatures which were close to the data reported by Murphy et al. on 8% ethanol [11]. Moreover, a mathematical model based on the Fick’s second law was validated to predict the extent of migration from the packaging material into the food simulant. An excellent fit between experimental and predicted values was obtained which allows its use to predicting migration at any time exposure.

References


