Study of the Migration of Stabilizer and Plasticizer from Polyethylene Terephthalate into Food Simulants

Bo Li¹,², Zhi-Wei Wang¹,²,*, Qin-Bao Lin¹,², and Chang-Ying Hu²,³

¹Packaging Engineering Institute, Jinan University, Zhuhai 519070, China, ²Key Laboratory of Product Packaging and Logistics of Guangdong Higher Education Institutes, Jinan University, Zhuhai 519070, China, and ³Department of Food Science and Engineering, Jinan University, Guangzhou 510632, China

*Author to whom correspondence should be addressed. Email: wangzw@jnu.edu.cn

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Abstract

This study investigates the determination and migration of stabilizers and plasticizers from polyethylene terephthalate (PET). Two methods [ultrasonic extraction with dichloromethane or methanol and total dissolution with phenol/tetrachloroethane (m:m/1:1)] for pre-concentration of additives in PET material were performed. The diffusion of these additives from PET was evaluated by immersing in deionized water, acetic acid 3% (w/v), ethanol 20% (v/v), ethanol 50% (v/v) and isooctane at 20, 40, 55 and 70°C, respectively. The amount of additives in PET and food simulants was quantified by high-performance liquid chromatography-photodiode array detector (HPLC-PDA). The optimized HPLC method showed high correlation coefficients (R ≥ 0.9993), good precision, accuracy and reproducibility. Experimental diffusion coefficients (Dₚ) were calculated according to a mathematical model based on Fick’s second law, and the Dₚ values of considered compounds ranged from 9.8 × 10⁻¹⁵ to 1.4 × 10⁻⁸ cm² s⁻¹. The experimental Dₚ values were also compared with that predicted by currently used diffusion models. In addition, the effect of temperature on the diffusion rate was assessed. The effect of temperature on the diffusion coefficients followed an Arrhenius-type model with active energies ranged from 40.4 to 113.8 kJ mol⁻¹ for the target compounds.

Introduction

Polyethylene terephthalate (PET) is a material that manufactured by polymerization of ethylene glycol and dimethyl terephthalate or terephthalic acid during a polycondensation reaction. In the last decades, the amount of PET in packaging applications increased significantly, and nowadays PET is the main packaging material for mineral water, beverages and oils. Besides, it is also used increasingly for packaging films as well as trays and dishes for microwave and conventional cooking. Even though PET is a highly inert packaging material, which means that the interactions between the material and the foodstuff are weak, there also have been some concerns about the migration of plastic components or additives that were used during manufacturing process.

Migrating compounds from packaging material to foods can be quantitatively determined by exposing the material in contact with food for specific time and temperature. Generally, the determination of migrating compounds into food under real conditions is quite difficult. This reason is that in most cases food simulants and special migration conditions takes place. European Union (EU) established regulations specifying migration tests using food simulants to determine the compounds probably migration into food. Testing migration conditions are currently described again in Regulation (EU) No. 10/2011 (1) that replaced old directives. The specific migration data can be obtained from migration tests carried out under controlled conditions of time and temperature of contact between the materials and food simulants.

Phthalate esters, light stabilizers based on benzotriazoles and antioxidants were reported to be used in the production of PET packaging (2, 3). Phthalate esters as plasticizers are principally used to increase the flexibility of polymers. Antioxidants and UV absorbers can delay the photolysis and photo-oxidation processes for PET degradation (4, 5).
However, the reported migrating compounds from PET are mainly concentrated on monomers (6, 7), antimony (8–10), formaldehyde, acetaldehyde (11–14), polymer degradation products (15) and other low-molecular-weight organic compounds (16); research about the migration of chemical additives from PET is relative rare. Until now, only a few researchers studied the migration of benzoazoles light stabilizers in PET (17, 18). Phthalate plasticizers were also reported into bottle water released from paper (19), polyvinyl chloride (20) and PET (21–24) packaging materials. To our knowledge, few studies have been published regarding the comparison of migration level of more than one kind of additives from PET material into different food simulants. The experimental values of key parameters of migration processes (diffusion coefficient and active energy) for additives in PET are also rare in the scientific literature.

An analytical method for simultaneous determination of 27 additives used in polymers has been developed in our previous work (25). As a further research, the present work was performed to study the migration of one antioxidant [2,6-di-tert-butyl-4-methylphenol (BHT)], two phthalate plasticizers [di-(2-ethylhexyl) phthalate (DEHP), dibutyl phthalate (DBP)] and three UV stabilizers [2-(2H-benzoazol-2-yl)-4,6-bis[1-methyl-1-phenylethyl]phenol (UV-234), (2’-hydroxy-3’,5’-tert-5’-methylphenyl)-5-chlorobenzo triazole (UV-326) and 2,2’-hydroxy-3,5’-methylphenyl)] from PET into diverse food simulants under different conditions; furthermore to determine the diffusion coefficient, partition coefficient and active energy values of the additives at different temperatures based on experimental test; and then to compare the diffusion coefficient values with that predicted by current commonly used diffusion models. The overall goal is to supply basic data that more closely approach the real value about migration of additives in PET packaging material, understand better the mechanisms of the migration process and the physicochemical properties that most influence this phenomenon, compare the experimental diffusion coefficient values with that predicted to estimate the security of the model prediction.

Experimental

Chemicals and reagents
The sources and some information of the model compounds are presented in Table 1. Methanol (HPLC grade) used as mobile phases in the HPLC was purchased from Merck (Darmstadt, Germany). Dichloromethane (A.R. grade), phenol (A.R. grade) and tetrachloroethane (A.R. grade) that were used for extraction solvents were obtained from Tianjin Kermel chemical reagent Co., Ltd (Tianjin, China). Acetic acid (A.R. grade) that were used for extraction solvents were obtained from Tianjin Kermel chemical reagent Co., Ltd (Tianjin, China). Ethanol (HPLC grade) and isooctane (HPLC grade) were obtained from Tianjin Kermel chemical reagent Co., Ltd (Tianjin, China). Formaldehyde, acetaldehyde, acetone, ethyl acetate, dichloromethane, ethyl alcohol (A.R. grade), phenol (A.R. grade) and tetrachloroethane (A.R. grade) that were used for extraction solvents were obtained from Tianjin Kermel chemical reagent Co., Ltd (Tianjin, China). Dichloromethane (A.R. grade), phenol (A.R. grade) and tetrachloroethane (A.R. grade) were obtained from Tianjin Kermel chemical reagent Co., Ltd (Tianjin, China). Acetic acid (A.R. grade) obtained was from Tianjin Kermel chemical reagent Co., Ltd (Tianjin, China). ethanol (HPLC grade) and isooctane (HPLC grade) were supplied from TEDIA (Cincinnati, OH, USA), and they were used as food simulant. High-purity deionized water (resistivity 18.2 MΩ cm

Instrumentation
The HPLC system was a Waters 2695 (Waters, Milford, MA, USA) equipped with a gradient pump, an automatic injector and a model 2996 UV photodiode array (Waters). LABUY-10LHT ultrasonic system (Hangzhou Labuy Industry Co., Ltd, Hangzhou, China) was used for the sample extraction. GZX-9420 MBE electric blast drying oven (Boxum Medical Equipment Industry Co., Ltd, Shanghai, China) was used for migration test. TurboVap™II evaporation system (Caliper Life Sciences Inc., Hopkinton, MA, USA) and QL-866 Vortex shaker (Haimen Qilinheiro Instrument Manufacturing Co., Ltd, Jiangsu, China) were used for sample concentration and homogenizing, respectively.

Preparation of standard solutions and calibrations
Primary stock solutions of DEHP, DBP and BHT were prepared with analytical accuracy dissolving 10 mg standard in 10 mL methanol (1,000 µg mL

PET test bottles
The chemicals dissolving in dichloromethane were mixed with virgin PET pellets and manufactured into particle by a twin-screw extrusion granulation line (Gangzhou PuTong Machinery and Equipment Manufacturing Co., Ltd, Guangzhou, China), subsequently blown to 250 mL PET bottles by Zhongfu Enterprise Co., Ltd (ZhuHai, China). The additives were added to PET material according to the maximum permitted amount. Bottles without additives were prepared under similar conditions by the same method and were used as controls. The thickness of samples were measured at five points spread out over the sample using a DRK 203B digital thickness meter (Derek Instrument Co., Ltd, Jinan, China), and the mean value of the samples were in the range of 0.215–0.239 mm. Density of the samples were in the range of 1.41–1.50 g cm

PET sample preparation
The initial content of chemical additives in PET sample were determined. PET bottle was cut into small pieces of ~0.5 × 0.5 cm, rinsed using ultrapure water and dried before extraction. Extraction solvent and blank PET bottle (without additives) were used as controls.

Ultrasonic extract with methanol
PET sample (1.0 g) was weighed, placed in a 100 mL conical flask with glass top and extracted with methanol (2 × 10 mL) by ultrasonic extraction for 30 min at 30°C. Additional 5 mL methanol was added to rinse the sample. Three extracts were mixed, gently shaken for 3 min and then filtered through a 0.22 µm pore-size nylon membrane filter. The concentration of BHT, DBP, DEHP, UV-P, UV-234 and UV-326 in PET bottle was analyzed by HPLC-photodiode array detector (HPLC-PDA).

Ultrasonic extract with dichloromethane
PET sample (1.0 g) was weighed, placed in a 100 mL conical flask with glass top and contacted overnight with 10 mL dichloromethane for maceration. Samples were mechanically shaken for 3 min and extracted for 30 min in an ultrasonic system at 30°C; extraction was then repeated once. The extracts were combined and evaporated to dryness under 40°C by a TurboVap™II evaporation system. The concentration was made up with methanol to an accurate volume of 2.0 mL, filtered
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Chemical name</th>
<th>Molecular weight</th>
<th>CAS No.</th>
<th>SML (µg g$^{-1}$)</th>
<th>Source</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV-P</td>
<td>2-(2′-Hydroxy-5′-methylphenyl)</td>
<td>225.25</td>
<td>2440-22-4</td>
<td>30.0</td>
<td>Sigma-Aldrich (Steinheim, Germany)</td>
<td><img src="image1.png" alt="Structure" /></td>
</tr>
<tr>
<td>UV-234</td>
<td>2-(2H-Benzotriazol-2-yl)-4,6- bis (1-methyl-1-phenylethyl)phenol</td>
<td>447.58</td>
<td>70321-86-7</td>
<td>1.5</td>
<td>AccuStandard, Inc. (New Haven, CT, USA)</td>
<td><img src="image2.png" alt="Structure" /></td>
</tr>
<tr>
<td>UV-326</td>
<td>(2′-Hydroxy-3′-tert-5′-methylphenyl)-5-chlorobenzotriazole</td>
<td>315.80</td>
<td>3896-11-5</td>
<td>30.0</td>
<td>AccuStandard, Inc. (New Haven, CT, USA)</td>
<td><img src="image3.png" alt="Structure" /></td>
</tr>
<tr>
<td>BHT</td>
<td>2,6-Di-tert-butyl-4-methylphenol</td>
<td>220.36</td>
<td>128-37-0</td>
<td>3.0</td>
<td>Fluka Cheme GmbH, Buchs Sigma- Aldrich (Augsburg, Germany)</td>
<td><img src="image4.png" alt="Structure" /></td>
</tr>
<tr>
<td>DEHP</td>
<td>Di-(2-ethylhexyl) phthalate</td>
<td>390.56</td>
<td>117-81-7</td>
<td>1.5</td>
<td>Sinapharm Chemical Reagent Co., Ltd (Shanghai, China)</td>
<td><img src="image5.png" alt="Structure" /></td>
</tr>
<tr>
<td>DBP</td>
<td>Dibutyl phthalate</td>
<td>278.34</td>
<td>84-74-2</td>
<td>0.3</td>
<td>Sinapharm Chemical Reagent Co., Ltd (Shanghai, China)</td>
<td><img src="image6.png" alt="Structure" /></td>
</tr>
</tbody>
</table>

through a 0.22 μm pore-size nylon membrane filter, and the concentration of six additives in PET bottle were analyzed by HPLC.

Dissolved with phenol/tetrachloroethane and extracted by methanol PET sample (1.0 g) was dissolved in 10 mL phenol/tetrachloroethane (m/m:1:1). The PET was precipitated from this solution using 30 mL methanol, added slowly from a burette and then extracted for 30 min in an ultrasonic system at 30°C. The solution was filtered through 0.45 and 0.22 μm filters, and the concentration of BHT, DBP, DEHP, UV-P, UV-234 and UV-326 was analyzed by HPLC.

During the ultrasonic extraction, aluminum foil was used to seal the conical flask with glass top to avoid solvent volatilization. Meanwhile, a mercury thermometer was used to monitor the temperature of water. There was no special processes to ensure the sample stayed at 30°C because the temperature fluctuation of water is not obvious during the ultrasonic process.

Specific migration tests

Regulation (EU) No. 10/2011 proposed ethanol 10% (v/v), acetic acid 3% (w/v), ethanol 20% (v/v), ethanol 50% (v/v) and vegetable oil as food simulants. Thinking of the difficulty of working with vegetable oil in HPLC systems and the main application in mineral water for PET, distilled water, acetic acid 3% (w/v), ethanol 20% (v/v), ethanol 50% (v/v) and isooctane were selected as food simulants in this work.

According to the literature, exposing rectangular strips to food simulants and total immersion was carried out (9, 18, 26–28). The strips were cut from PET bottle with a scissor using a rectangular template measuring—care was taken to cut them all in a uniform size (3.0 x 4.0 cm)—and placed in a glass vial with cap containing 20 mL food simulants. The vials were then hermetically closed and stored in electric blast drying oven at 20, 40, 55 or 70°C. Migration investigations (kinetic measurements) were carried out at various specific times until migration equilibrium. For nonfatty food simulants [distilled water, acetic acid 3% (w/v), ethanol 20% (v/v) and ethanol 50% (v/v)], an aliquot (1.0 mL) of simulated was taken from the vial, cooled to room temperature and analyzed directly. For fatty food simulant, isoctane was transferred into a glass tube and evaporated to dryness, redissolved in 2.0 mL methanol and finally analyzed by HPLC-PDA.

In all experiments, the migration conditions were as follows: 20°C for 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 days (all food simulants) 40°C for 2, 4, 6, 9, 12, 16, 20, 24, 36 and 48 h (all food simulants) 55°C for 2, 4, 6, 9, 12, 16, 20, 24, 36 and 48 h (all food simulants) 70°C for 20, 40, 60 and 90 min and 2, 4, 6, 9, 12, 16, 20 and 24 h (isooctane) 70°C for 2, 4, 6, 9, 12, 16, 20 and 24 h [distilled water, acetic acid 3% (w/v), ethanol 20% (v/v) and ethanol 50% (v/v)]

Migration tests were performed separately; there were separate test solutions for each temperature and time point. The concentration of chemicals that migrated into food simulant was calculated by the following equation:

\[ C_{\text{migration}} = \frac{C_{\text{simulant}} \times V_{\text{simulant}}}{m_{\text{simulant}}} \]  

where \( C_{\text{migration}} \) is the concentration of chemicals from the PET into food simulant (µg g\(^{-1}\)), \( C_{\text{simulant}} \) is the concentration of chemicals found in food simulant (µg mL\(^{-1}\)), \( V_{\text{simulant}} \) is the volume of food simulant (mL) and \( m_{\text{simulant}} \) is the quantity of food simulant (g). These values were selected to determine the kinetic performance of the samples as described elsewhere.

The simulant of each sample was analyzed in triplicate. A blank prepared with only simulant and another with blank PET bottle (without additives) strip in food simulant were used as reference, exposed and analyzed under the same conditions.

HPLC-PDA analysis

The amount of additives in PET samples and food simulants was determined by HPLC. Separations were achieved using an X Bridge™ C18 column (250 mm x 4.6 mm, 5 µm) from Waters. Chromatographic separation was carried out using a gradient elution with methanol/water binary mixture; the initial proportion was 80% methanol/20% water (v/v), then linear gradient up to 95% methanol/5% water (v/v) at 10 min, to 100% methanol within the next 10 min, and returned to the initial conditions in 5 min. The total run time was 25 min. The flow rate was 1.0 mL min\(^{-1}\), and the injection volume was 20 µL. The column temperature was maintained at 30°C. The wavelength in the PDA detector was set at 275 nm. Each compound was identified by comparison of its retention time with corresponding peak in the standard solution and its UV spectrum.

Kinetics analysis of additives migration from PET

Calculation of the partition coefficients of additives in PET

The partition coefficient was estimated from the experimental data considering the final values of concentration as being close to equilibrium. \( C_{\text{P,in}} \) and \( C_{\text{F,in}} \) are the concentrations of compound in PET and food simulants at equilibrium, respectively.

\[ K_{PF} = \frac{C_{\text{F,in}}}{C_{\text{P,in}}} \]  

Calculation of the diffusion coefficients of additives in PET

To quantify the extension of the migration process from PET, mathematical model based on Fick’s second law [Equation (3)] was used (27, 29–31). This differential equation is useful for describing the migration of an additive or contaminant from packaging material:

\[ \frac{\partial C_p}{\partial t} = D_p \frac{\partial^2 C_p}{\partial x^2} \]  

where \( C_p \) is the concentration of the migrant in the polymer (P) at time \( t \) and position \( x \) in P. \( D_p \) is the diffusion coefficient in polymer.

In our particular case, to enable use of this model in the case of the PET–food simulants under study, an effective diffusion coefficient \( D_{ep} \) for the whole PET–food simulants system rather than only polymer was included. Equation (3) can be resolved to express the amount of migrant released from the PET (P) into food simulant (F) at time \( t \) and expressed as:

\[ \frac{M_{PF,t}}{M_{PF,\infty}} = 1 - \sum_{n=1}^{\infty} \frac{2a(1+a)}{1 + a + a^2 q_n^2} \exp \left( -D_{ep} \frac{q_n^2}{2} \frac{t}{d_F} \right) \]  

\[ a = \frac{1}{K_{PF} V_F} \]  

where \( M_{PF,t} \) is the amount of migrant from polymer into the foodstuff or simulants at time \( t \). \( M_{PF,\infty} \) is the amount of migrant from polymer into the foodstuff or simulants at equilibrium. The diffusion coefficient of the migrant is \( D_p \), and \( t \) is the storage time. The thickness of the packaging material is \( d_F \). The factor \( a \) [Equation (5)] contains the partition coefficient \( K_{PF} \), and the volumes of the food simulant and packing (\( V_F \) and \( V_p \)). The term \( q_n \) is the positive square roots of the equation \( \tan q_n = -\alpha \cdot q_n \).
The parameters including \( d_p \), \( V_T \) and \( V_F \) are easily available in this work. The concentration of migrant in food simulants at each specific time point and at equilibrium can be determined experimentally by HPLC. The partition coefficients (\( K_{F,fi} \)) of the additives were calculated from the experimental data according to Equation (2). Model parameter \( \sigma \) was calculated according to Equation (5). The term \( q_n \) was calculated from the equation \( q_n = -\alpha \cdot q_m \). The greater the number of roots, the more reliable the results are. Nevertheless, because of the considerable amount of work involved in the calculation, and to make the estimation feasible, 10 roots (\( 1 \leq n \leq 10 \)) were calculated. The diffusion coefficient \( D_f \) was determined through a nonlinear regression (nlin-fit) by MATLAB R2012a (MathWorks, Natick, MA, USA) to fit the experimental data base on Equation (4).

Estimated diffusion coefficients with current diffusion models

Related researchers have reported a series of sophisticated models for theoretical estimation of diffusion coefficients; the most commonly used was Piringer’s model, proposed by Piringer et al. Another model proposed by Limm and Hollifield was also used to estimate the diffusion coefficient of low-molecular-weight organic compounds in PET [16].

Piringer’s diffusion models expressed as (32):

\[
D_f = 10^4 \exp \left( A_P - 0.1351M_f^{1/3} + 0.003M_r - \frac{10,454}{T} \right) \quad (6)
\]

\[
A_P = A_p^2 - \frac{R}{T} \quad (7)
\]

Piringer introduced a so-called \( A_P \) parameter. This dimensionless \( A_P \) parameter is a simplified numerical representation of a given polymer for quantifying its diffusion behavior. \( A_P \) is also a function of temperature independent according to Equation (7). The use of certain \( A_P \) and \( T \) is a major simplification. Recent activities coordinated by the EU to update and refine migration models have proposed to adapt \( A_P \) values for PET to 3.1 at temperatures below the glass transition temperature \( (T_g) \) of ~70°C and to 6.4 above \( T_g \) (33). Both values are used in combination with \( r = 1,577 \ K \).

Limm’s diffusion model expressed as (34):

\[
\ln D_f = \ln A - \alpha (M_f)^{1/2} - K (M_r)^{1/3} \quad (8)
\]

\( D_f \) is the diffusion coefficient of a compound in polymer, \( M_f \) is the molecular weight of the compound, \( T \) is the temperature (K), and \( \ln A, \alpha \) and \( K \) are the constants determined from experimental data. The values for \( \ln A, \alpha \) and \( K \) for PET are 8.88, -1.04 and 2,859, respectively.

Calculation of the active energies of additives in PET

The active energies of diffusion are typically derived from the correlation between the logarithm of the experimentally determined diffusion coefficient and the reciprocal temperature (in K) according to Equation (9) (Arrhenius approach).

\[
D_f = D_0 \cdot e^{-E_a/(R \cdot T)} \quad (9)
\]

where \( D_0 \) is a constant, \( E_a \) is the active energy (J mol\(^{-1}\)), \( R \) is the universal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)), and \( T \) is the absolute temperature (K). The parameters \( D_0 \) and \( E_a \) can be obtained by curve fitting of the experimental data.

Statistical analysis

Statistical analysis was carried out using Statistical Product and Service Solutions (SPSS) 16.0 (IBM SPSS Inc., New York, NY, USA) statistical software. \( p \)-value <0.05 was identified as being statistically significant at the 95% confidence level.

Results

Analytical features for quantitative analysis method

The presented method was validated for linearity, limit of detection (LOD), limit of quantitation (LOQ), accuracy, repeatability and stability under the optimum conditions. Peak areas were employed throughout the validation procedure for the calculation of the concentration. Standard solutions were injected from low concentration to high concentration to perform the standard curve. The studied chemicals responses were found to be linear over the concentration range (0.1–20.0 \( \mu g \) mL\(^{-1}\)). LOD and LOQ were determined as the signal at 3 and 10 times the height of the noise level. Serially diluted standard mixture solutions were injected or spiked from high concentration to low concentration to estimate the LODs and LOQs of the analytes. Purity angle test was also carried out to judge the purity of the peaks obtained. The LODs, LOQs, purity angle and purity threshold of the target compounds are presented in Table II.

Recovery test was carried out by standard addition procedure. The achieved recoveries of six analytes in blank PET sample were between 71.2 and 96.8% with relative standard deviations (RSDs) lower than 9% at concentration of 20, 80 and 200 \( \mu g \) g\(^{-1}\). The recoveries in food simulants are in the range of 70.3–114.6% at concentration of 0.5, 1.0 and 2.0 \( \mu g \) mL\(^{-1}\), with RSDs between 1.0 and 12.6% (Table III). Each analytical sequence was composed of solvent blanks, calibration standards, reference blank samples (virgin PET or food simulants) and samples (PET or food simulants) that spiked the target chemicals. Experiments were performed in triplicate from sample preparation to HPLC analysis.

Intra-day and inter-day variations were chosen to determine the stability of the chemicals in solution and simulant. Experiments were performed in six replicates. Good results were obtained for

| Additive | Retention time (min) | Slope ± SD | Intercept ± SD | Linearity range (\( \mu g \) mL\(^{-1}\)) | Correlation coefficient(R) | Purity angle (Purity threshold) | LOD, LOD\(^M\) (\( \mu g \) mL\(^{-1}\), \( \mu g \) g\(^{-1}\)) | LOQ, LOQ\(^M\) (\( \mu g \) mL\(^{-1}\), \( \mu g \) g\(^{-1}\)) |
|----------|---------------------|------------|----------------|------------------|--------------------------|---------------------------|-----------------|-----------------|----------------|
| DBP      | 7.14 ± 0.02         | 5.427 ± 28 | 516 ± 374      | 0.2–20.0         | 0.9993                   | 0.462 (0.684)          | 0.05, 4.80      | 0.15, 16.00     |
| UV-P     | 9.29 ± 0.03         | 32.381 ± 204| 597 ± 858       | 0.1–20.0         | 0.9999                   | 0.343 (0.463)          | 0.03, 1.50      | 0.10, 5.00      |
| BHT      | 10.37 ± 0.03        | 10.182 ± 90 | 663 ± 500       | 0.1–20.0         | 0.9998                   | 0.712 (1.081)         | 0.04, 4.20      | 0.12, 14.00     |
| DEHP     | 15.46 ± 0.03        | 4.640 ± 10 | 721 ± 126       | 0.2–20.0         | 0.9995                   | 0.849 (1.183)         | 0.05, 6.40      | 0.15, 20.00     |
| UV-234   | 18.25 ± 0.03        | 12,814 ± 91 | 666 ± 399       | 0.1–20.0         | 0.9998                   | 0.582 (0.671)         | 0.04, 3.60      | 0.12, 12.00     |
| UV-326   | 19.15 ± 0.04        | 17,721 ± 129| 348 ± 842       | 0.1–20.0         | 0.9999                   | 0.591 (0.601)         | 0.04, 3.00      | 0.12, 10.00     |

LOD\(^2\), LOD\(^M\), the LOD of the instrument and the LOD of the method; LOQ\(^2\), LOQ\(^M\), the LOQ of the instrument and the LOQ of the method.
almost all of the tests, and the RSDs were <12% (Table IV). A quintessential chromatogram of the selected six chemicals (10 µg mL$^{-1}$ standard solution) is shown in Figure 1a1, and HPLC chromatogram of the standard solution at the concentration of 0.05 µg mL$^{-1}$ (LOD of the target additives) is shown in Figure 1a2.

Chemicals concentration in PET bottle

The concentration of chemical additives in PET bottle is presented in Table V. It was observed that there was no UV-326 found. It is likely that UV-326 precipitated from the solution during the pelletizing and extrusion process for its low solubility and not added in the PET bottle. It is agreement with the reports of Monteiro et al. (17) and Nerín et al. (35), which proved that UV-326 is not soluble and difficult to incorporate into PET. As shown in Column 2 of Table V, only DBP, UV-P, BHT were detected, and the concentration was very low; it indicated that methanol was unsuitable for extracting these additives from PET. Columns 3 and 4 of Table V are the concentration of additives obtained by ultrasonic extract with dichloromethane and dissolved with phenol/tetrachloroethane, five additives were all detected from PET bottle. Afterwards, independent-samples t-test was used to compare the concentration of additives obtained by the two methods at a 95% confidence level. Analytical results have shown that there was a statistical difference in extraction efficiencies for the two methods, and dissolved the material with phenol/tetrachloroethane has contributed to the extraction of additives. The typical HPLC chromatograms of extracted solutions of PET bottle (with additives) and blank PET bottle (without additives) are shown in Figure 1b1 and b2.

Migration levels

To evaluate the migration level of the additives, migration studies were performed at four temperatures (20, 40, 55 and 70°C) over a wide range of time. A large amount of migration data was obtained. The test results show large differences in the migration level of additives among the five kinds of food simulants. It was found that there was no additives migrated into deionized water and 3% (w/v) aqueous acetic acid at 70°C; the same has occurred at other temperatures.

Table III. Recoveries and Precision for Spike of the Six Additives in Blank PET and Food Simulants (n = 3)

<table>
<thead>
<tr>
<th>Fortified concentration</th>
<th>DBP</th>
<th>UV-P</th>
<th>BHT</th>
<th>DEHP</th>
<th>UV-234</th>
<th>UV-326</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank PET</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 µg g$^{-1}$</td>
<td>76.4 (1.8)</td>
<td>71.4 (1.7)</td>
<td>76.2 (7.9)</td>
<td>85.3 (8.2)</td>
<td>78.5 (5.0)</td>
<td>71.2 (3.7)</td>
</tr>
<tr>
<td>80 µg g$^{-1}$</td>
<td>82.3 (2.2)</td>
<td>88.0 (1.8)</td>
<td>75.2 (2.8)</td>
<td>93.0 (4.3)</td>
<td>82.1 (6.7)</td>
<td>83.6 (4.2)</td>
</tr>
<tr>
<td>200 µg g$^{-1}$</td>
<td>83.4 (3.1)</td>
<td>96.8 (1.9)</td>
<td>85.6 (7.8)</td>
<td>83.8 (4.7)</td>
<td>85.5 (5.8)</td>
<td>83.0 (4.1)</td>
</tr>
</tbody>
</table>

Table IV. Intra- and Inter-day Stability of Six Additives in Solution and Isooctane (n = 6)

<table>
<thead>
<tr>
<th>Concentration (µg mL$^{-1}$)</th>
<th>RSD of concentration (%) intra-day/inter-day</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DBP</td>
</tr>
<tr>
<td>Solution</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>3.2/11.1</td>
</tr>
<tr>
<td>2.0</td>
<td>5.4/4.1</td>
</tr>
<tr>
<td>10.0</td>
<td>3.0/2.4</td>
</tr>
<tr>
<td>Isooctane</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>3.1/7.3</td>
</tr>
<tr>
<td>2.0</td>
<td>1.5/5.9</td>
</tr>
<tr>
<td>10.0</td>
<td>5.5/4.9</td>
</tr>
</tbody>
</table>

Chemicals concentration in PET bottle

The concentration of chemical additives in PET bottle is presented in Table V. It was observed that there was no UV-326 found. It is likely that UV-326 precipitated from the solution during the pelletizing and extrusion process for its low solubility and not added in the PET bottle. It is agreement with the reports of Monteiro et al. (17) and Nerín et al. (35), which proved that UV-326 is not soluble and difficult to incorporate into PET. As shown in Column 2 of Table V, only DBP, UV-P, BHT were detected, and the concentration was very low; it indicated that methanol was unsuitable for extracting these additives from PET. Columns 3 and 4 of Table V are the concentration of additives obtained by ultrasonic extract with dichloromethane and dissolved with phenol/tetrachloroethane, five additives were all detected from PET bottle. Afterwards, independent-samples t-test was used to compare the concentration of additives obtained by the two methods at a 95% confidence level. Analytical results have shown that there was a statistical difference in extraction efficiencies for the two methods, and dissolved the material with phenol/tetrachloroethane has contributed to the extraction of additives. The typical HPLC chromatograms of extracted solutions of PET bottle (with additives) and blank PET bottle (without additives) are shown in Figure 1b1 and b2.

Migration levels

To evaluate the migration level of the additives, migration studies were performed at four temperatures (20, 40, 55 and 70°C) over a wide range of time. A large amount of migration data was obtained. The test results show large differences in the migration level of additives among the five kinds of food simulants. It was found that there was no additives migrated into deionized water and 3% (w/v) aqueous acetic acid at 70°C; the same has occurred at other temperatures.
Figure 1. HPLC chromatograms of mixed standard solution, extracted solution and food simulants. (a1) Mixed standard solution at the concentration of 10 µg mL$^{-1}$, (a2) mixed standard solution at the concentration of 0.05 µg mL$^{-1}$ (LOD of the target additives), (b1) extracted solution of PET bottle (with additives), (b2) extracted solution of blank PET bottle (without additives), (c) ethanol 20% (v/v) after 24 h of contact with the PET bottle (with additives) at 70°C, (d) ethanol 50% (v/v) after 24 h of contact with the PET bottle (with additives) at 70°C and (e) isooctane after 24 h of contact with the PET bottle (with additives) at 70°C. [(1) DBP, (2) UV-P, (3) BHT, (4) DEHP, (5) UV-234 and (6) UV-326].
In 20% (v/v) aqueous ethanol, additives have not migrated at 20 and 40°C. Only UV-P has been found at 55°C, while DBP and UV-P have migrated at 70°C. In 50% (v/v) aqueous ethanol, more kinds of additives have migrated with the temperature increased. At 20 and 40°C, only UV-P was found, whereas four additives (DBP, UV-P, BHT and DEHP) migrated at 55°C and all the target chemicals were detected at 70°C. In isooctane, four additives have migrated from PET material at the four temperatures except BHT. The maximum migration amounts of additives obtained at different temperatures in diverse food simulants are summarized in Figure 2. Figure 1c–e shows the HPLC chromatograms of different simulant solutions after migration equilibrium of direct contact with the PET bottle (with additives), while the HPLC chromatograms of simulants blank are shown in the Supplementary material online, Figures S1–S5. Paired t-test was performed to compare the maximum migration amounts of additives from PET into different food simulants at a 95% confidence level. The results of statistical analysis (P < 0.05) indicated that the maximum migration amounts of DBP and UV-P into aqueous ethanol were significantly higher than into isooctane, and the amount tends to increase with greater percentage of ethanol in solution. Meanwhile, the maximum migration amount of DEHP into isooctane was significantly higher than into ethanol 50% (v/v).

### Key migration parameters

The key parameters have been calculated for all model migrants into food simulants except aqueous food simulants due to the low water solubility for migrants. $K_{PF}$ and $D_T$ of the different migrants can be calculated.

### Table V. Concentration of the Additives Achieved in PET Bottle Using Different Preparation Methods (n=3)

<table>
<thead>
<tr>
<th>Additive</th>
<th>Concentration of additives in samples (average ± SD, µg g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Methanol (ultrasonic extraction)</td>
</tr>
<tr>
<td>DBP</td>
<td>46.2 ± 1.2</td>
</tr>
<tr>
<td>UV-P</td>
<td>34.4 ± 1.8</td>
</tr>
<tr>
<td>BHT</td>
<td>30.3 ± 1.5</td>
</tr>
<tr>
<td>DEHP</td>
<td>–</td>
</tr>
<tr>
<td>UV-234</td>
<td>–</td>
</tr>
<tr>
<td>UV-326</td>
<td>–</td>
</tr>
</tbody>
</table>

**Figure 2.** Maximum migration amounts of additives from PET into different food simulants at various temperatures. (a) Migrate into ethanol 20% (v/v), (b) migrate into ethanol 50% (v/v) and (c) migrate into isooctane [(1) the migration of DBP, UV-P and UV-234; and (2) the migration of DEHP].

**Table V.** Concentration of the Additives Achieved in PET Bottle Using Different Preparation Methods (n=3)
according to Equations (2) and (4) described above. Furthermore, plot the 

diagrams of $\ln D_T$ against $1/T$ according to the experimental 
data, and then obtain $E_a$ of the additives. The experimental and predicted 
values of migration parameters for five additives are presented in Table VI. 
The experimental $D_T$ values ranged from 1.3 x 10^{-12} to 9.6 x 10^{-11} 
cm^2 s^{-1} for DBP, 8.4 x 10^{-13} to 1.1 x 10^{-10} cm^2 s^{-1} for UV-P, 2.1 x 10^{-11} to 
3.3 x 10^{-11} cm^2 s^{-1} for BHT, 5.8 x 10^{-12} to 1.4 x 10^{-9} cm^2 s^{-1} for 
DEHP and 9.8 x 10^{-13} to 8.9 x 10^{-12} for UV-234 in various food simulants 
within a temperature range of 20 and 70°C. The diffusion of UV-P from PET bottle (with additives) into ethanol 50% (v/v) at 70°C and 
DEHP into isooctane at 55°C according to the Fick’s second law is 
shown in Figure 3. Table VII presents the active energies of additives in 
PET according to the Arrhenius equation.

**Discussion**

**Influencing factor for kinetic migration**

From the results obtained, the influencing factors for the migration of 
chemical compounds are type of food simulant, migration time, 
temperature, the molecular weight and structure of the migrant.

**Effect of different food simulants on the migration**

The results show large differences in the migrated amount depending 
on the type of food simulant. Migration of chemical compounds to 
aqueous and acidic food simulants was under the LOD and could 
not be detected, while significant migration occurred to the aqueous 
ethanol and fatty food simulants. Moreover, the kind of migrated 
chemical tends to increase with greater percentage of ethanol in the 
food simulant. For instance, only DBP and UV-P have migrated into 
20% (v/v) aqueous ethanol at 70°C, while five target additives have 
migrated into 50% (v/v) aqueous ethanol at the same temperature. 
The maximum migration amount for DBP and UV-P were 2.0 and 
1.3 times higher in 50% (v/v) aqueous ethanol, respectively, than in 
20% (v/v) aqueous ethanol. Meanwhile, significant migration has 
occurred in isooctane at the temperature from 20 to 70°C. This could be 
explained by high affinity of ethanol and isooctane to PET, which 
causes swelling of the polymer and facilitates migration as well as by 
the solubility of the additives into the food simulant. The migration 
into aqueous food simulant was in most cases under detection limits, 
which is probably due to the limited solubility of the hydrophobic 
additives into the aqueous simulant.

**Effect of time and temperature on the migration**

The extent of migration of chemical from PET material to food simul-
ulant related to the effects of migration time and temperature. As ex- 
pected, under experimental conditions with increasing time and 
temperature, migration of additives into food simulants has increased 
gradually until equilibrium. In order to understand the role of storage 
time and temperature more comprehensively, Figure 4 shows their

---

Table VI. Migration Parameters for Additives in PET at Various Temperatures and Food Simulants

<table>
<thead>
<tr>
<th>Food simulant</th>
<th>Additive</th>
<th>Temperature (°C)</th>
<th>$K_{P,F}$</th>
<th>$\alpha$</th>
<th>$D_{P,exp}$ (cm² s⁻¹)</th>
<th>$D_{P,lim}$ (cm² s⁻¹)</th>
<th>$D_{P,Pir}^{lim}$ (cm² s⁻¹)</th>
<th>$D_{P,Pir}^{exp}$ / $D_{P,Pir}^{lim}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol 20% (v/v)</td>
<td>DBP</td>
<td>70</td>
<td>3,163</td>
<td>0.026</td>
<td>1.2 x 10⁻¹¹</td>
<td>5.9 x 10⁻¹³</td>
<td>9.6 x 10⁻¹³</td>
<td>2.6 x 10⁻¹¹</td>
</tr>
<tr>
<td></td>
<td>UV-P</td>
<td>55</td>
<td>19,050</td>
<td>0.005</td>
<td>3.1 x 10⁻¹¹</td>
<td>4.1 x 10⁻¹³</td>
<td>3.5 x 10⁻¹³</td>
<td>9.5 x 10⁻¹²</td>
</tr>
<tr>
<td></td>
<td>Ethanol 50% (v/v)</td>
<td>DBP</td>
<td>55</td>
<td>3,427</td>
<td>0.025</td>
<td>3.4 x 10⁻¹¹</td>
<td>4.9 x 10⁻¹⁴</td>
<td>1.9 x 10⁻¹³</td>
</tr>
<tr>
<td></td>
<td>UV-P</td>
<td>20</td>
<td>55,971</td>
<td>0.002</td>
<td>8.4 x 10⁻¹³</td>
<td>7.3 x 10⁻¹⁶</td>
<td>4.4 x 10⁻¹⁵</td>
<td>1.2 x 10⁻¹³</td>
</tr>
<tr>
<td></td>
<td>BHT</td>
<td>55</td>
<td>9,388</td>
<td>0.009</td>
<td>2.1 x 10⁻¹¹</td>
<td>5.1 x 10⁻¹³</td>
<td>3.7 x 10⁻¹³</td>
<td>1.0 x 10⁻¹¹</td>
</tr>
<tr>
<td></td>
<td>DEHP</td>
<td>55</td>
<td>9,628</td>
<td>0.009</td>
<td>5.8 x 10⁻¹²</td>
<td>1.3 x 10⁻¹⁵</td>
<td>6.3 x 10⁻¹⁴</td>
<td>1.6 x 10⁻¹²</td>
</tr>
<tr>
<td></td>
<td>UV-234</td>
<td>70</td>
<td>16,643</td>
<td>0.005</td>
<td>8.9 x 10⁻¹²</td>
<td>5.4 x 10⁻¹⁵</td>
<td>1.9 x 10⁻¹³</td>
<td>5.1 x 10⁻¹²</td>
</tr>
<tr>
<td>Isooctane</td>
<td>DBP</td>
<td>20</td>
<td>16,808</td>
<td>0.005</td>
<td>1.3 x 10⁻¹²</td>
<td>5.5 x 10⁻¹⁷</td>
<td>2.4 x 10⁻¹⁵</td>
<td>6.6 x 10⁻¹⁴</td>
</tr>
<tr>
<td></td>
<td>UV-P</td>
<td>20</td>
<td>190,500</td>
<td>0.001</td>
<td>9.2 x 10⁻¹³</td>
<td>7.3 x 10⁻¹⁶</td>
<td>4.4 x 10⁻¹⁵</td>
<td>1.2 x 10⁻¹³</td>
</tr>
<tr>
<td></td>
<td>DEHP</td>
<td>20</td>
<td>1,454</td>
<td>0.057</td>
<td>1.1 x 10⁻¹¹</td>
<td>6.6 x 10⁻¹⁹</td>
<td>7.9 x 10⁻¹⁶</td>
<td>2.1 x 10⁻¹⁴</td>
</tr>
<tr>
<td></td>
<td>UV-234</td>
<td>20</td>
<td>187,000</td>
<td>0.001</td>
<td>9.8 x 10⁻¹⁵</td>
<td>1.0 x 10⁻¹⁹</td>
<td>4.7 x 10⁻¹⁶</td>
<td>1.3 x 10⁻¹⁴</td>
</tr>
</tbody>
</table>

\[ a_T = 3.1. \]

\[ a_T = 6.4. \]
Isooctane DBP 65.6 0.9831
Ethanol 50% (v/v) UV-P 78.4 0.9648

represents the mass of additive migrated at time $t$ divided by the mass of additive migrated at equilibrium. The $x$-axis describes $t$ as time in s. The symbols (plus, circle and triangle) represent the three replicate experimental data and the solid lines are the values from Equation (4).

<table>
<thead>
<tr>
<th>Food simulant</th>
<th>Additive</th>
<th>$E_a$ (kJ mol$^{-1}$)</th>
<th>Correlation coefficient/R</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol 50% (v/v)</td>
<td>UV-P</td>
<td>78.4</td>
<td>0.9648</td>
</tr>
<tr>
<td></td>
<td>DBP</td>
<td>65.6</td>
<td>0.9831</td>
</tr>
<tr>
<td></td>
<td>UV-P</td>
<td>40.4</td>
<td>0.9680</td>
</tr>
<tr>
<td></td>
<td>DEHP</td>
<td>113.8</td>
<td>0.9677</td>
</tr>
<tr>
<td></td>
<td>UV-234</td>
<td>97.3</td>
<td>0.9678</td>
</tr>
<tr>
<td>Isooctane</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 3. Diffusion of UV-P from PET into ethanol 50% (v/v) at 70°C (a), and DEHP from PET into isooctane at 55°C (b) according to the Fick’s second law. The $y$-axis represents the mass of additive migrated at time $t$ divided by the mass of additive migrated at equilibrium. The $x$-axis describes $t$ as time in s. The symbols (plus, circle and triangle) represent the three replicate experimental data and the solid lines are the values from Equation (4).

Effects on concentration of migrated UV-P, DBP and DEHP into aqueous ethanol and isooctane within a temperature range of 40 and 70°C, respectively. In fact, migration phenomena relate to time-dependent factors such as diffusion and permeation. Studies have confirmed the effect of increasing storage time on enhancing the concentration of migrants (13, 17, 36–38). Hence, greater migration of additives occurred with increasing the exposure time. The temperature factor seems to have a direct influence on both rate and extent of migration. As shown in Figure 4, increased temperatures lead to higher migration rates and rapid establishment of equilibrium. A very likely explanation is that raising the temperature provides the required energy level for chemicals to begin migration and increases the diffusion coefficient and permeability of chemicals (39). Other explanation is that the diffusion enhancement is due to greater segmental motions of polymeric chains at higher temperature, which results in increasing the size of free volume (40).

Effect of the characteristic and molecular weight of the chemical

The characteristics of the migrant usually have a significant impact on the migration route. As an example, the amount of DEHP that migrated from PET into isooctane was greater than other additives, and more DEHP migrated into isooctane than aqueous ethanol. This is because molecules with similar polarities tend to be attracted to each other. Isooctane is a nonpolar solvent, and the polar of DEHP is weaker than others, allowing DEHP partially dissolve in isooctane. In addition, the diffusion of migration molecules in polymer also strongly depends on the size and molecular weight of the migrant. Arvanitoyannis and Stratakis (41) reported that high molecular weight and complex molecular configurations (spherical oriented molecules, molecules with side chains) are resulted in lower levels of migration. According to free volume theory, polymer matrix can be considered to consist of the volume occupied by the polymer molecules and the unoccupied free volume. Additive molecules diffuse in polymer matrix through the free volume voids, and the free volume plays a vital role in diffusion. It can be seen from Table I, UV-234 has a higher molecular weight and more complex configuration than other additives, which means it needs larger free volume to diffuse; the inherently lower migration amounts of it are supportive to our findings.

Parameters that may influence $K_{P,F}$, $D_P$ and $E_a$

The partition coefficient, which is the relative solubility of the migrant at equilibrium between the plastic and the food simulant, was calculated with the polymer and food simulant volumes. $K_{P,F}$ values of the considered additives in every system were much larger than 1 (Table VI). It indicates that a higher concentration of migrant remained in PET relative to the food simulant after reaching equilibrium. It seems that there is a close relationship between temperature and $K_{P,F}$ value; the values decreased gradually as the temperature increased for a certain compound into the same simulant.

Temperature and molecular weight of the chemical and food simulants have been correlated with the diffusion coefficients. We have already verified that migration is influenced by temperature, and after calculating $D_P$, we have also verified that temperature has a positive correlation with this key migration parameter. The influence of molecular weight of the chemical in the migration process was found in our work, which has concluded that the higher is the molecular weight, the slower are diffusion rates. In most of the cases, UV-234 presented the lower diffusion coefficients than DBP and UV-P in the same situation; this is probably due to the higher molecular weight of this substances compared with DBP and UV-P. Diffusion coefficients are also dependent on food simulant; in the cases of DBP and UV-P at 70°C, the higher is the amount of ethanol in the simulant, the higher is $D_P$. This might happen due to a swelling phenomenon of the polymer in the presence of the ethanol simulant.

In general, $E_a$ value is influenced by the range of temperatures tested and it is applicable only in that range. The $E_a$ values observed for UV-P from PET into ethanol 50% (v/v) and isooctane were 78.4 and 40.4 kJ mol$^{-1}$, respectively, within a temperature range of 20 and 70°C. It indicated that the type of food simulant also has an effect on the active energy of migrant. The Arrhenius plots of the experimentally
determined diffusion coefficients on temperature in PET of UV-P and DEHP were constructed and these appear in Figure 5.

Correlation between experimental and modeled diffusion coefficients
The $D_p$ values in every system were calculated based on Fick’s second law and compared with the values predicted by Limm’s and Piringer’s diffusion models (Table VI). The results showed that the predicted $D_p$ values by Limm’s diffusion model were all less than the experimental values. Specifically, Piringer’s model, as the most commonly used diffusion model, the predicted $D_p$ values are generally within one or two orders of magnitude of the experimental $D_p$ for most conditions when $A_p$ set 6.4 (except DEHP into isooctane). Nevertheless, when $A_p$ set 3.1, the $D_p$ values predicted by Piringer’s model were all less than the experimental values. Welle and Franz (42) evaluated literature data for diffusion coefficients of small molecules over the specific...
range of 18–130 g mol⁻¹ in PET at 35–40°C. They found that for small molecules, the predicted $D_P$ values from Piringer’s model with an $A_P$ value of 3.1 are lower than the diffusion coefficients derived from experimental studies. It is evident that the model with the revised modeling parameter for PET below its $T_g$ ($A_P = 3.1$) does not provide the margin of safety for the prediction of diffusion coefficients in PET. This is in excellent agreement with the result determined in this study. The phenomenon that experimental $D_P$ values of DEHP into isooctane within the temperature range of 20 and 70°C are much greater than that predicted is much interesting. The migration of DEHP from PET into isooctane is appreciable in a short time. From our perspective, Piringer’s diffusion model focuses on the chemical and polymer material merely, not consider the property of food or food simulant. The food or food simulant probably plays an important role on the migration of chemical substance when the substance is easily dissolved in the simulant, and the application of Piringer’s model would be restricted at this time. For clearer mechanism, a more detailed investigation should be done in further studies.

Strengths and weaknesses

A series of work about the migration of stabilizer and plasticizer from PET into different food simulants were carried out in this paper. It was contributed to supply basic data for the migration of chemical additives from PET material. Within the limitations of migration testing, further work is required, especially on the migration of additives into real foodstuffs. In addition, although migration test was performed by strip cut and total immersion instead of article filling in some research, there are some concerns about the affection of edge effect, which may enlarge the surface in contact with the simulants and overestimate the migration values. The investigation about influencing mechanism and overvalued degree should also be done in future work.

Conclusion

In this study, an effective method was developed to determine stabilizer and plasticizer from PET by HPLC-PDA. It showed good linearity, precision, repeatability, stability and accuracy. Dissolving the PET sample with phenol/tetrachloroethane (m:m/1:1) was demonstrated an effective way to promote the extraction of additives from PET bottle. This preparation method may not only limit to the additives in this study, but can also be applied in routine analysis for the determination of the content of other additives in polymer material.

The migration of stabilizer and plasticizer from PET into food simulants [deionized water, acetic acid 3% (w/v), ethanol 20% (v/v), ethanol 50% (v/v) and isooctane] was evaluated at different temperatures and times, using HPLC-PDA to determine the concentration of chemical additives in simulants. The recovery of additives from spiked food simulants was good, and the detection of them by HPLC was precise and accurate. The kinetic migration experiments confirmed the importance of physicochemical properties of both model migrant and food simulants. The temperature also seems to influence the mass transport processes. In all the kinetics performed on food simulants, the combination of a high temperature and a long migration time helped the migration of additives from PET material.

The good correlation between experimental and predicted results by Piringer’s diffusion model indicates that this model can be used to predict $D_P$ values, but the input parameter of model ($A_P$) with a value of 6.4 is better than 3.1 at the low temperature for PET below its $T_g$. For the compound easily dissolved in food simulant, simulants probably play a more important role on the migration process, which resulted in the restriction of the application of Piringer’s model.

Supplementary material


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References