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Migration behavior of photoinitiators in polyethylene-coated paper for takeaway fast food

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ORIGINAL ARTICLE

Abstract

The migration of photoinitiators (PIs): benzophenone (BP), ethyl 4-dimethylaminobenzoate (EDAB), and 4-chlorobenzophenone (CBP), from polyethylene (PE)-coated paper to 4% (v/v) acetic acid and 10% (v/v) salt-simulated food solution was quantitatively analyzed using gas chromatography–mass spectrometry. The migration behavior of the three PIs was studied under three specific working conditions: conventional heating, microwave power, and random vibration level. The migration rate of the three PIs in acidic food simulants was ranked from BP > EDAB > CBP under the specific working conditions. The mobility of the three PIs increased with increasing temperature, microwave power, and random vibration acceleration in 4% (v/v) acetic acid by 10, 10, and 15%, respectively. The experimental migration data of three PIs in PE-coated paper under different temperatures and microwave powers were used to establish the Crank monolayer migration model according to Fick's second law. The diffusion coefficient D increased with an increase in experimental conditions. According to the migration data under the condition of random vibration level, a mathematical model conforming to the Fick model was established, fitting the migration process. These results showed that conventional heating, microwave heating, and vibration could affect the food safety of PE-coated paper.

Keywords: diffusion model; migration; PE-coated paper; photoinitiator; takeout fast food; random vibration

Introduction

The food processing industry selects packaging materials according to food requirements. Packing in plain paper is insufficient for food products because of poor barrier properties, low heat sealability, and low strength (Amini *et al*., 2016). The protection of paper-based packaging is ensured through additional coating layers. The purpose of the coating is to create the conditions that a particular packaging needs (Mujtaba *et al*., 2022). So, it is impregnated with some additive or laminated with aluminum or plastic to improve its functional properties, and is often done industrially through lamination with a polymer (Deshwal *et al*., 2019). Cellulosic fibers, such as paper and paperboard, have traditionally been used in packaging for a wide range of food categories, such as dry food products, frozen or liquid foods, beverages, and even fresh foods (Samyn, 2021; Spence *et al*., 2010). The U.S. production of paper food service ware, including molded pulp fiber containers, exceeds 1.4 Mt (Glenn *et al*., 2021).

In April 2018, the Shanghai Quality Supervision Bureau released the country's first group standard for takeaway delivery boxes. This standard can facilitate the

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use of coated paper bowls in place of plastic delivery boxes, which can reduce plastic waste by more than 75% (Shanghai publishes, 2018). Thus, the use of polyethylene (PE)-coated paper in takeaway fast food packaging material has increased rapidly in the fast food industry. The main base material for coated paper has great properties, low consumption of oil resources, and is better waterproof and oilproof. However, the safe use of the coated paper still lacks effective verification. Ink adsorption and photoinitiator (PI) migration from the coated papers may cause food safety risks. PIs are components of ultraviolet-curable printing inks and varnishes that trigger polymerization reactions in the curing process, which becomes a contaminant in food plastic packaging printing (Elizalde *et al*., 2020). PIs can migrate from the external printing surface to the interior of the packaging material under certain conditions, and the toxicity level also varies which makes the issue more complex (Ji *et al*., 2019). Some of these PIs are classified as toxic, reprotoxic, and cancerogenic (Chen *et al*., 2022). Several factors, including food composition, temperature, contact time (Arvanitoyannis and Kotsanopoulos, 2014), packaging material, packaging content, molecular weight, polarity, and lipophilicity of the relevant additives, can influence the migration of hazardous substances in coated paper (Aparicio and Elizalde, 2015). The migration of relevant chemical substances in packaging materials has become a major public concern.

Several studies on food contact materials have focused on the migration behavior of fluorescent brighteners (Ji *et al*., 2020), antioxidants (Kang *et al*., 2018; Yang *et al*., 2016), heavy metals (Jiang *et al*., 2019; Peng *et al*., 2020), and phthalate plasticizers (Prasannan *et al*., 2017) in single-use plastic packaging materials. Because of the difficulty in directly analyzing and detecting the migrating components in foods, suitable food simulants are selected for alternative studies (Lago *et al*., 2019; Van Den Houwe *et al*., 2016). Furthermore, several studies (Li *et al*., 2015) have investigated the extraction and chromatographic parameters suitable for rapid extraction of PI (Zhang *et al*., 2016) and simultaneous determination of multiple PI (Liu *et al*., 2016). The development of analytical methods for the quantitative determination of relevant PIs in food packaging materials is very important.

The complex environmental conditions, such as transportation bumps, high temperatures, humidity, and microwave heating during the delivery process, facilitate the migration of hazardous substances in PE-coated paper for takeaway fast food. A nationwide survey of the dietary characteristics of takeout containers or takeaway containers using an online questionnaire suggested that attention should be paid to the potential hazards of plasticizers in the use of takeout containers (Wang *et al*., 2021).

The effect of ambient temperature, refrigeration, and different exposure methods on benzophenone (BP) migration into food from carton packaging materials have been investigated. The result showed that the attenuation effects of indirect exposure and low-temperature storage were cumulative (Anderson and Castle, 2003). A mathematical model based on Fick's second law was used to study the migration dynamics of two PIs to food simulants at freezing temperatures (Lago *et al*., 2019). The mathematical model was solved numerically using the finite element method. The finite element provides more flexibility in the numerical analysis to meet a wider range of applications in working conditions (Hao *et al*., 2017). Currently, the study on the migration of PIs from packaging paper to food focuses mainly on the effects of temperature and microwave factors. In contrast, there is no relevant research on the migration pattern of PIs in the food distribution process and the effect of transport vibrations on the migration of hazardous substances on PE-coated paper during fast food delivery.

The objective of this study was to evaluate the migration patterns of BP, ethyl 4-dimethylaminobenzoate (EDAB), and 4-chlorobenzophenone (CBP) to acidic and neutral food simulants under three specific conditions: conventional heating, microwave heating, and random vibration. The effects of temperature, microwave power, and acceleration level on the migration rates of PIs were analyzed. In addition, the migration rates of PIs to different types of food simulants were compared. A mathematical model was developed to predict the migration behavior of PIs in PE-coated paper based on the experimental data and relevant parameters. This study can effectively assess the safety of coated paper and provide reference and guidance to PE-coated paper (particularly for food packaging) manufacturers and relevant regulatory agencies.

Materials and Methods

Samples, standards, and chemical reagents

Food packaging paper samples are commercially available coated paper delivery boxes with a volume of 500 mL, a weight of 7.68 g, and a coating layer of 0.3 mm thick. The lid of the matching set was made of polypropylene (PP) and obtained from market vendors.

Benzophenone (BP, ≥ 98%), ethyl 4-dimethylaminobenzoate (EDAB, ≥ 98%), 4-chlorobenzophenone (CBP, ≥ 98%) were purchased from Baiotai Technology Co., Tianjin.

Methanol (GC), acetic acid (GC), and hexane (GC) were purchased from Keshang Experimental Equipment Distribution Department, Tianjin. The water used in the experiments was tertiary deionized water.

Instruments and equipment

The following instruments were used: QP2010ULTRA-AOC-5000 gas chromatograph (Shimadzu, Kyoto, Japan), ME3002T/02 electronic analytical balance accurate up to 1 mg, (Mettlertoledo, Shanghai, China), vortex mixer (Huxi Industrial Co., Shanghai, China), KQ-800DE intelligent ultrasonic oscillator (Ultrasonic Instruments Co., Kunshan, China), DHG-9123A electrothermal blast dryer (Yiheng Scientific Instruments Co., Shanghai, China), HH-2 digital display thermostat water bath (Munters Instrument Manufacturing Co., Changzhou, China), RWBZ-08S microwave dynamic extraction equipment (Suenry Drying Equipment Co., Nanjing, China), and DC-600-6 vibration test bench (Sushi Test Instruments Co., Suzhou, China).

Experimental methods

Gas chromatography–mass spectrometry parameter settings

The gas chromatograph (SN / T 4265-2015) was equipped with an RTX-17 MS 50% diphenyl 50% dimethylsiloxane (30.0 m × 0.25 mm × 0.25 μm) capillary column with high purity helium (purity 99.999%) as carrier gas. The ramp-up procedure was as follows: the starting temperature was set at 60°C and held for 1 min, increased to 180°C at 20°C/min for 3 min, then increased to 250°C at 5°C/min for 1 min, and finally increased to 290°C at 20°C/min for 3 min. The sample volume was 1 μL (injected without splitting), the inlet temperature was 260°C, the pressure was 57.4 kPa, the flow rate was 1.0 mL/min, and the solvent delay time was 6 min.

Mass spectrometry was performed under the following conditions: ion source temperature (220°C), interface temperature (220°C), ionization method using electron bombardment (EI source), electron energy (70 eV), and SIM ion scanning mode.

Paper sample preparation

The previously reported method of paper sample processing was adjusted (Huang *et al*., 2020) as follows: (1) the original paper sample was cut into 3 × 2 cm size paper samples; (2) a standard mixture solution of 1000 mg/L of BP, EDAB, and CBP was prepared; and (3) the 3 × 2 cm paper samples were soaked in the prepared solution for 12 h. Then, the paper samples were removed from the solution and dried in a fume hood for 3 h. Finally, the paper samples were removed from the fume hood for migration experiments.

Eight sheets were randomly selected from the above-dried paper samples and were cut into small pieces of 0.5 × 0.5 cm. Hexane (3 mL) was added to the samples, and the extract was collected through ultrasonication for 30 min and vortexed for 3 min. The experiment was repeated 3 times. Afterward, the extract was filtered through a 0.22-μm organic filter membrane and injected into GC-MS for detection. The initial content was calculated using Eqs. (1).

$$M_{P,0} = \frac{C_0 \times V_0}{S} \quad (1)$$

where $M_{P,0}$ is the initial content of the paper sample, C_0 is the initial concentration of the measured paper sample (μg/mL), V_0 is the volume of the sample after constant volume (mL), and S is the area of the paper sample (dm^2).

Migration experiments

According to the relevant standards of the Food and Drug Administration, the European Union, and the National Standard of China, 4% (v/v) acetic acid solution and 10% (v/v) salt solution were selected as acidic food simulant A and neutral food simulant B, respectively, in this experiment.

The migration experiments were performed at different temperatures: 40, 60, 80, and 100°C using a thermostat water bath. Samples were taken at 30-, 60-, 90-, 120-, 180-, and 300-min intervals. Three parallel samples were set up for each group of experiments, with a blank control.

In addition, migration experiments were performed at three microwave power level conditions: 400, 600, and 800 W, using microwave dynamic extraction equipment. Six contact times (5, 10, 15, 20, 25, and 30 s) were tested at each of the three microwave wattage levels during the migration tests.

Moreover, migration experiments were performed at different random vibration conditions. A vibration testing machine was used to simulate the process of take-away fast food transportation. The migration test was conducted according to GB/T 4857.23-2012 "Basic test for transport package Part 23: random vibration test method." Three acceleration level conditions of ASTM D4169-16 random vibration were selected. The power spectral density curves data for random vibration are shown in Table 1. The vibration time was set at 15, 30, 60, 90, and 120 min to remove the samples. The sample without vibration treatment was used as a blank.

After the migration experiment, 10 mL of hexane was added to the food simulant. The mixture was subjected to vortex-assisted extraction for 3 min and ultrasonic shaking for 30 min. Then, the mixture was allowed to stand for 15 min, after which the supernatant was separated. Subsequently, 1 μL of the solution to be measured was passed through a 0.22-μm organic filter membrane, and the filtrate was analyzed via GC-MS. The migration rate was used to express the relative migration levels under

Table 1. Datasheet for power spectral density curve.

Frequency/Hz	Power spectral density/(g²/Hz)		
	Level I	Level II	Level III
1	0.0001	0.00005	0.000025
4	0.02	0.01	0.005
16	0.02	0.01	0.005
40	0.002	0.001	0.0005
80	0.002	0.001	0.0005
200	0.00002	0.00001	0.000005
Root Mean Square (RMS) value of acceleration (grms)	0.73	0.52	0.37

specific working conditions. The migration rate was calculated using Eqs. (2).

$$\text{Migration rate } (\%) = \frac{M_{F,t}}{M_{P,0}} \times 100 \quad (2)$$

where $M_{F,t}$ is the PI migration in the food simulant at moment t, mg/dm².

Development of migration model

Migration is a diffusion process. The Crank's (Barton, 1975) Eqs. (3) and (4) derived from Fick's second law were calculated using migration experimental data of three PIs, with the key parameters: partition coefficient $K_{P/F}$ and diffusion coefficient D.

$$\frac{M_{F,t}}{M_{F,\infty}} = 1 - \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)}{0+\alpha+\alpha^2 q_n^2} \exp\left[\frac{q_n^2 Dt}{L_p^2}\right] \quad (3)$$

$$\alpha = \frac{V_F}{V_P K_{P/F}} = \frac{M_{F,\infty}}{M_{P,0} - M_{F,\infty}} \quad (4)$$

where $M_{F,\infty}$ is the migration of the PI in the food simulant at equilibrium (mg/dm²), L_p is the thickness of the coated paper (cm), D is the diffusion coefficient of the PI (cm²/s), q_n is the non-zero positive root of the equation $\tan q_n = -\alpha - q_n$, α is the mass ratio of migration in the simulant to migration in the packing paper at equilibrium, and $K_{P/F}$ is the partition coefficient.

Results and Discussion

Linearity, limit of detection, and limit of quantification

Quantitative analysis of the sample was performed using the external standard method. The mixed standard stock solutions of 10, 20, 40, 60, 80, and 100 mg/L in the above steps were prepared in a series for analysis. The standard curve and linear equations for each substance were obtained by fitting the graph with the different concentrations of the substances as the horizontal coordinate X and the peak area response value as the vertical coordinate Y.

Table 2. Linear equations and LOD for the three photoinitiators.

PIs	Rt/ min	Linear equations	R^2	LOD/ (mg·L⁻¹)	LOQ/ (mg·L⁻¹)
BP	12.440	Y = 166726x – 2E + 06	0.99	0.1	0.3
EDAB	13.577	Y = 82927x – 2E+ 06	0.99	0.2	0.6
CBP	15.552	Y = 88611x – 3E+ 06	0.99	0.3	0.9

BP, benzophenone; EDAB, ethyl 4-dimethylaminobenzoate; CBP, chlorobenzophenone.

According to the ACS guidelines (Macdougall *et al*., 1980), the signal-to-noise ratio S/N = 3 was calculated as the limit of detection (LOD) of the instrument and S/N = 10 as the limit of quantification (LOQ). The retention times (Rt), linear equations, correlation coefficients (R^2), LOD, and LOQ for the three PIs are shown in Table 2. The initial contents of PIs in the paper samples were determined using the method described in Section 2.3.2. The initial contents of BP, EDAB, and CBP were 29.29 ± 2.54, 53.21 ± 3.67, and 41.52 ± 2.98 mg/dm², respectively.

Migration of three photoinitiators at different temperatures

Effect of temperature on the migration

Migration is the transfer of a compound from the packaging material to the food in contact, where the migrating component diffuses until the chemical potentials of the two phases of the packaging material and the food are in equilibrium (Garde *et al*., 2001). Figure 1 shows the migration behavior curves of the three PIs in two different food simulants (A and B). The migration rates of the four PIs gradually increased with increasing experimental migration time and temperature. The migration rates reached equilibrium after 180 min. For example, the migration rates of BP, EDAB, and CBP were approximately 10% higher at 100°C than at 40°C, implying that the migration rate at 40°C < the migration rate at 60°C < the migration rate at 80°C < the migration rate at 100°C. This temperature response trend is consistent with the theory of molecular thermal motion and similar to the results of previous studies. An increase in temperature resulted in the expansion of the volume

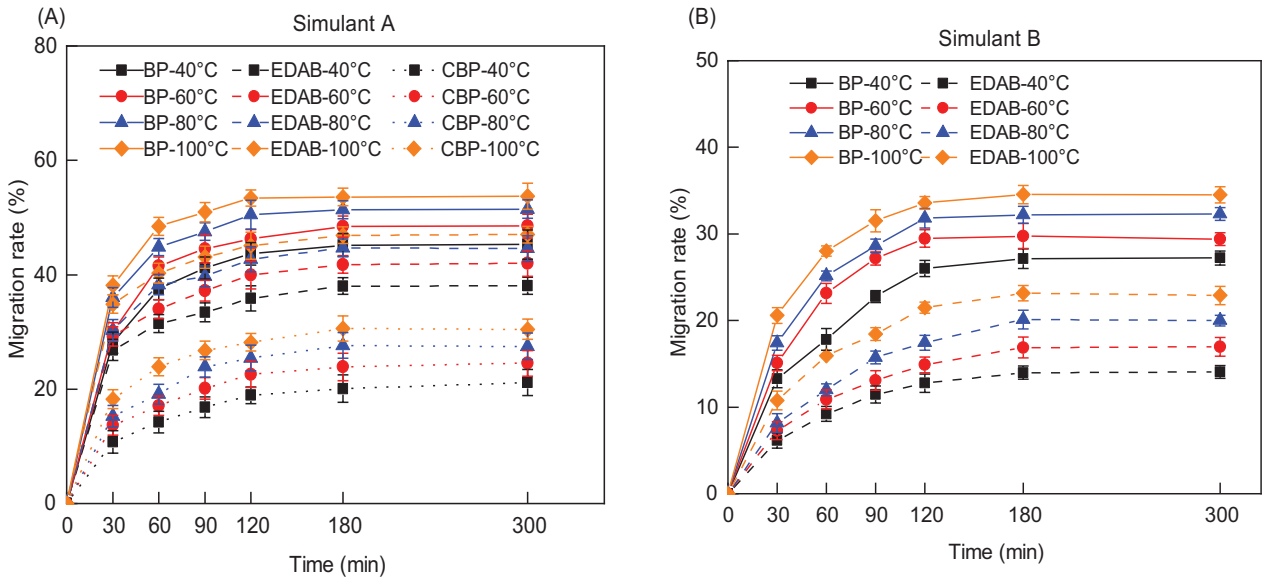

Figure 1. Migration of three PIs to different food simulants A and B at different temperatures: 40, 60, 80, and 100°C.

of the PE-coated paper-based polymer, accelerating the diffusion of PIs.

Figure 2 shows the equilibrium migration rates of three PIs in the two food simulants: A and B. The result showed that the PI in the coated paper is more likely to migrate into the acidic simulant. Thus, the solubility of PI in neutral food simulants was low, reducing the migration rate. A previous study (Zabaleta *et al.*, 2020) showed that the migration process depends on the nature of the migrant and the food. The migration rates of the three PIs in the acidic food simulant were ranked from BP > EDAB > CBP, with similar properties. However, the differences in their molecular masses and chemical structures led to different migration rates. The molecular weights of BP, EDAB, and CBP are 240, 193, and 216 respectively. This conclusion was consistent with the conclusion arrived at in the previous study (Feigenbaum *et al.*, 1994). That study concluded that substances with smaller relative molecular masses migrate faster from food packaging papers to the food in contact owing to the different spatial structures of the molecules and the different activity strengths of their molecular chain segments. Thus, the migration process can be difficult or easy, depending on the relative molecular mass of the substance (Lago *et al.*, 2019).

Model development and application

The migration of the three PIs occurred under four different temperature conditions: 40, 60, 80, and 100°C. The Crank migration model with known temperature conditions and equations (3) and (4) was applied to calculate the α values, partition coefficients ($K_{p/F}$), and diffusion coefficients (D) for BP, EDAB, and CBP in the three different food simulants.

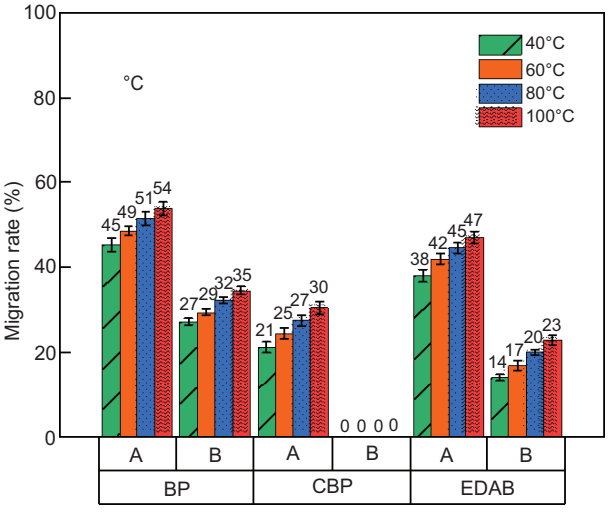

Figure 2. Equilibrium migration rates of the three photoinitiators in simulants A and B.

The overall linearity of migration fit the three food simulants with R^2 > 0.9 (Table 3). The diffusion coefficients of BP, EDAB, and CBP increased with increasing temperature, while the partition coefficient decreased with increasing temperature. A similar conclusion was reached in a study (Paseiro-Cerrato *et al.*, 2018) on the migration of relevant additives from low-density PE films to cake samples. The neutral food simulant has a poor affinity for PE-coated paper, little swelling effect, and a small diffusion coefficient D. However, the acidic stimulants are more likely to cause swelling of the coated paper material to penetrate and diffuse into the food, increasing diffusion coefficients and PIs migration rates. To verify

Table 3. Diffusion coefficients of the three photoinitiators at different temperature conditions.

Photoinitiators	Food simulants	Temperature(°C)	α	$K_{P/F}$	D/(cm²·s⁻¹)	R²
BP	A	40	0.28	197.85	4.19E-10	0.996
		60	0.37	151.02	4.99E-10	0.998
		80	0.47	119.04	5.77E-10	0.991
		100	0.56	98.43	6.67E-10	0.992
	B	40	0.07	790.89	1.07E-10	0.994
		60	0.10	556.84	1.64E-10	0.990
		80	0.17	332.79	1.96E-10	0.996
		100	0.21	266.66	2.40E-10	0.999
EDAB	A	40	0.29	189.34	2.86E-10	0.982
		60	0.36	152.45	3.46E-10	0.985
		80	0.42	131.58	4.10E-10	0.990
		100	0.49	113.94	4.73E-10	0.980
	B	40	0.07	828.01	2.92E-11	0.980
		60	0.10	571.21	3.90E-11	0.986
		80	0.17	331.05	4.24E-11	0.994
		100	0.19	291.73	8.01E-11	0.992
CBP	A	40	0.11	509.46	6.57E-11	0.998
		60	0.15	377.84	9.50E-11	0.998
		80	0.25	221.58	1.28E-10	0.992
		100	0.35	160.12	1.74E-10	0.998

BP, benzophenone; EDAB, ethyl 4-dimethylaminobenzoate; CBP, chlorobenzophenone.

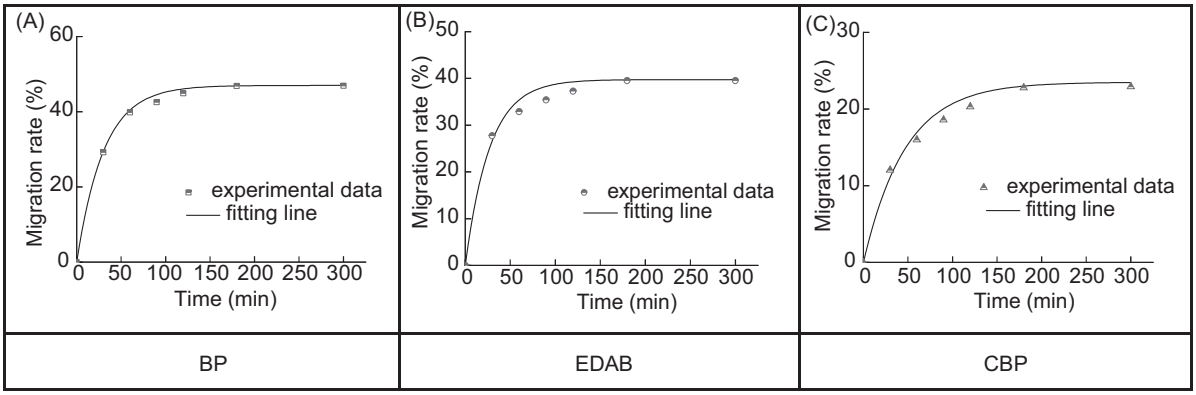

Figure 3. Predicted migration of three photoinitiators (BP, EDAB, CBP) to 4% acetic acid at 50°C.

the feasibility of the model, the migration of the three PIs in 4% acetic acid was predicted at 50°C. The model prediction curves shown in Figure 3 were in good agreement with the experimental data.

Migration of three PIs at different microwave powers

Effect of microwave power on the migration

The trends of the migration rates of the three PIs into the two food simulants A and B at different microwave powers are shown in Figure 4. As the microwave heating time increased, the migration rate increased until an equilibrium state was reached. Increasing microwave power shortened the PIs migration time and equilibrium time. The decrease in PIs migration time and equilibrium time was because the increase in microwave power could lead to an increase in the kinetic energy of the small molecules of PI in the packaging material and an increase in the number of small molecules with diffusion activation energy, thus increasing their diffusion rate. Microwave heating can effectively accelerate the migration of PIs more than conventional heating; because the increase in microwave power has a greater impact on the movement of polar molecules, it is easier to accelerate the movement of polar molecules (Ji *et al.*, 2019).

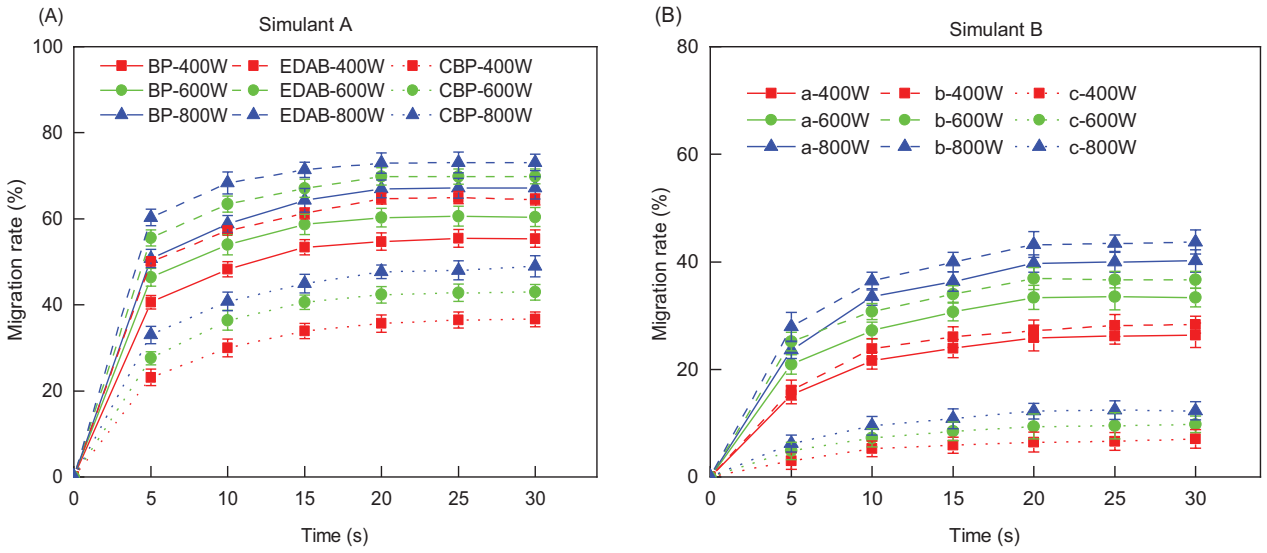

Figure 4. Migration of three photoinitiators to different food simulants A and B at different microwave powers 400, 600, and 800 W.

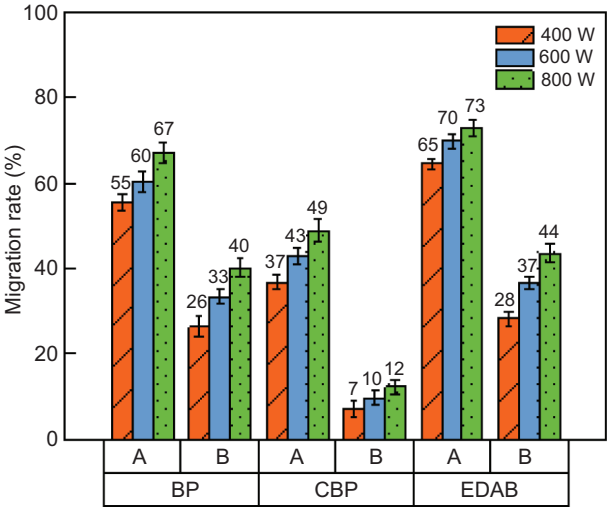

Figure 5. Equilibrium migration rates of the three photoinitiators in simulants A and B.

Figure 5 shows the equilibrium migration rates of the three PIs to different food simulants. The equilibrium migration rates of BP, EDAB, and CBP at the maximum power of 800 W were approximately 10% higher than that at the minimum power of 400 W. At a higher frequency of microwaves and molecular rotation, high power promotes the rotation and movement of molecules; thus, smaller molecules are separated from the packaging material system and migrate to the food. The equilibrium migration rate of BP, EDAB, and CBP in simulant A was 25, 30, and 35% more than in simulant B, respectively, at 800 W. In general, the smaller the values of relative molecular mass, oil-water partition coefficient and boiling point, the easier it is to move out of food packaging paper and more likely it is to cause harm to food safety (Han *et al.*, 2016).

Model development and migration prediction

The migration behavior of PIs under common microwave power conditions has a similar pattern to that of temperature conditions. Therefore, the experimental data of BP, EDAB, and CBP at 400, 600, and 800 W microwave power was used to build a migration model using the Crank model to calculate the distribution coefficient and diffusion coefficient of three PIs in PE-coated paper. From the data in Table 4, the PI diffusion coefficient D at 400 W was significantly smaller than that at 600 W. The partition coefficient $K_{P/F}$ decreases with increasing power. A larger value of $K_{P/F}$ indicates difficulty in transferring small PI molecules, affecting the migration rate. The developed models and the derived equations show the direct correlation between migration and the partition coefficient $K_{P/F}$ and between polymer and food (Ernstoff *et al.*, 2017). Similar results have been reported for the positive correlation between power and this key migration parameter. The migration model was used to predict the migration of the three PIs in 4% acetic acid at a microwave power of 500 W. The predicted data was in good agreement with the experimental data (Figure 6).

Migration of three PIs at different random vibration levels

Effect of random vibration levels on the migration

Figure 7 shows the migration kinetic curves of BP, EDAB, and CBP in the acidic and neutral food simulants under

Table 4. Diffusion coefficients of the three photoinitiators at different power conditions.

PIs	Food simulants	Power/W	α	$K_{P/F}$	D/(cm²·s⁻¹)	R²
BP	A	400	0.59	94.21	2.39E-10	0.998
		600	0.90	61.49	2.97E-10	0.999
		800	1.60	34.86	3.54E-10	0.998
	B	400	0.12	463.46	5.10E-10	0.995
		600	0.21	264.90	8.57E-10	0.998
		800	0.31	178.55	1.17E-09	0.991
EDAB	A	400	1.25	44.40	3.30E-10	0.998
		600	1.89	29.35	4.01E-10	0.993
		800	5.89	9.44	4.60E-10	0.998
	B	400	0.03	1867.74	2.83E-11	0.982
		600	0.04	1243.72	5.94E-11	0.994
		800	0.06	948.86	9.76E-11	0.990
CBP	A	400	0.30	187.60	9.24E-11	0.986
		600	0.42	131.49	1.34E-10	0.985
		800	0.54	103.27	1.68E-10	0.996
	B	400	0.03	1867.74	2.83E-11	0.982
		600	0.04	1243.72	5.94E-11	0.994
		800	0.06	948.86	9.76E-11	0.990

BP, benzophenone; EDAB, ethyl 4-dimethylaminobenzoate; CBP, chlorobenzophenone.

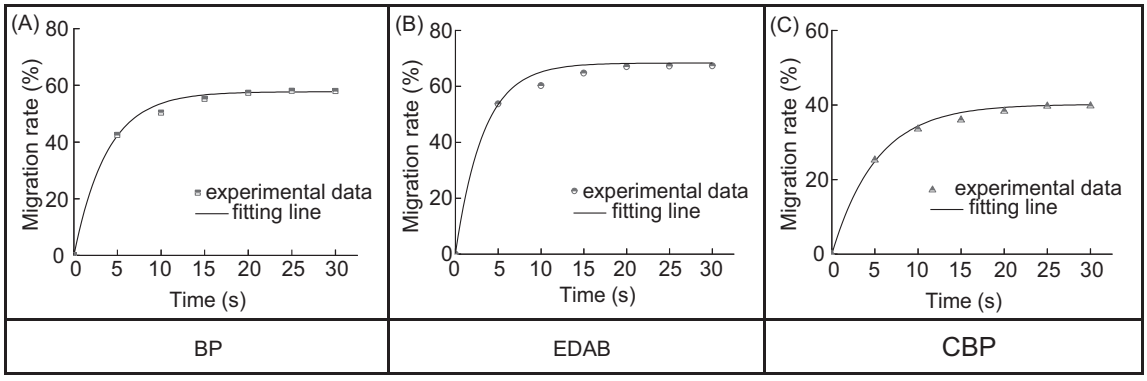

Figure 6. Predicted migration of three photoinitiators (BP, EDAB, CBP) to 4% acetic acid at 500 W.

random vibration levels I, II, and III. During contact with the food simulant, the PIs maintained their relatively independent chemical properties; they migrated from the coated paper over time and dissolved into the food, contaminating the food (Li *et al.*, 2016). After migration reaches an equilibrium state, the migration rate remains constant.

Figure 8 compares the equilibrium migration rates of the three PIs into the acidic food simulant under different random vibration level conditions. The equilibrium mobility under level I conditions increased by approximately 5 and 10% compared to the equilibrium migration rates under levels II and III, respectively. This increment showed that the vibration acceleration level played an important role in the migration of the PI from the food packaging paper to the food. The higher the acceleration level, the greater the migration, and the shorter the migration equilibrium time. For different kinds of food simulants, the migration rules of various PIs under three random vibration conditions show that under the same migration time conditions, the mobility of A is higher

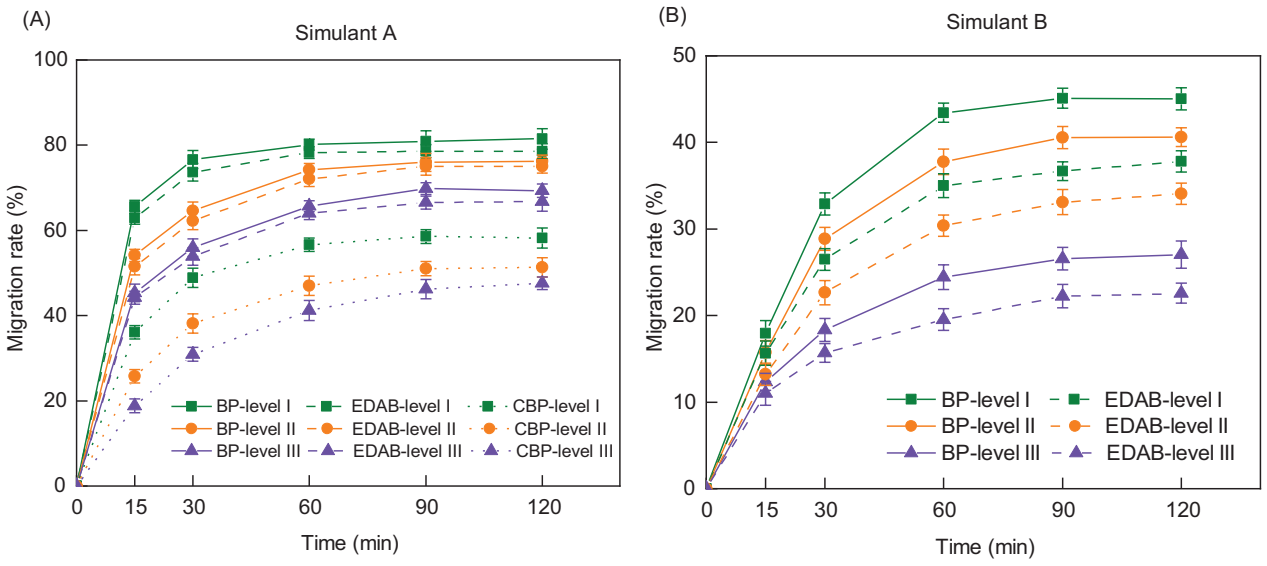

Figure 7. Migration of three photoinitiators to different food simulants A and B at different random vibration levels I, II, and III.

than that of B, and the highest mobility of BP, CBP, and EDAB is 81, 58, and 79%, respectively. This phenomenon can be attributed to the destructive effect of acetic acid molecules in the acidic food simulant on the coated paper (SN / T 4265-2015). Due to the deterioration of the inner coated layer, a portion of the relevant PI in the coated paper delivery box was released into the food at an accelerated rate. A similar migration behavior was observed in the migration pattern of the three PIs in the same class of food simulants with the same migration sequence: BP > EDAB > CBP. The difference in the migration rates can be attributed to the difference in the chemical structure of the PIs and their solubility. The properties of Physicochemical, such as molecular weight, polarity, and lipophilicity of the PI, played a vital role in the migration process. The PE coating layer has a strong holding effect on the CBP, thus restricting its release.

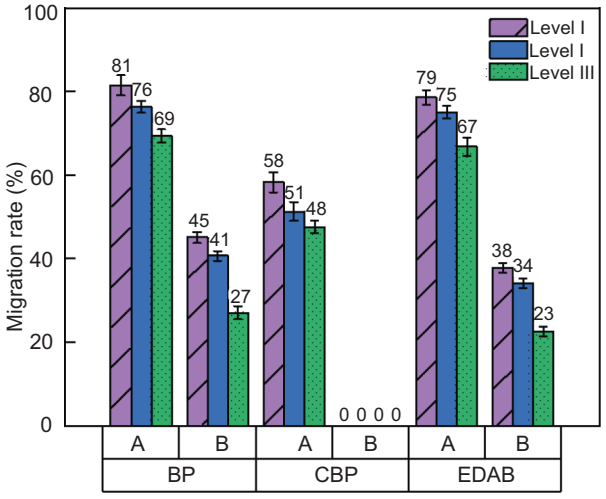

Figure 8. Migration of the three photoinitiators in simulants A and B.

Establishing mathematical models for PI migration

The migration kinetic curves of PIs under different random vibration levels had similar trends to the above two conditions. The Crank model cannot be applied to calculate the distribution coefficients because the change in random vibration level changed the contact area between the food simulant and the PE-coated paper. Thus, the evaluation of the migration of PIs on coated paper becomes more complex. To the best of our knowledge, there are a few studies on PIs migration rates under random vibration level conditions with molecular mechanisms different from simple diffusion. The nonlinear curve fitting of the relevant experimental data based on the Fick model using Origin software and the values of each parameter $M_{F,\infty}$, A, and b in the model obtained from the nonlinear fit are shown in Table 5. The mathematical equations (5) (6), and (7) of the migration models for BP, EDAB, and CBP, respectively, were developed by establishing the relationship equations between the random vibration levels and each parameter and replacing each parameter with the relationship equations. Figure 9 shows the mathematical model equations: (5), (6), and (7), that were used to fit the experimental data for the migration of the three PIs into 4% acetic acid and 10% salt solutions at three random vibration levels. The results showed that the R^2 values were greater than 0.99, indicating a good fit. The equation can only predict PI migration behavior for RMS acceleration values between 0.37 and 0.73. This study showed that random vibration influenced PI migration from the PE-coated paper.

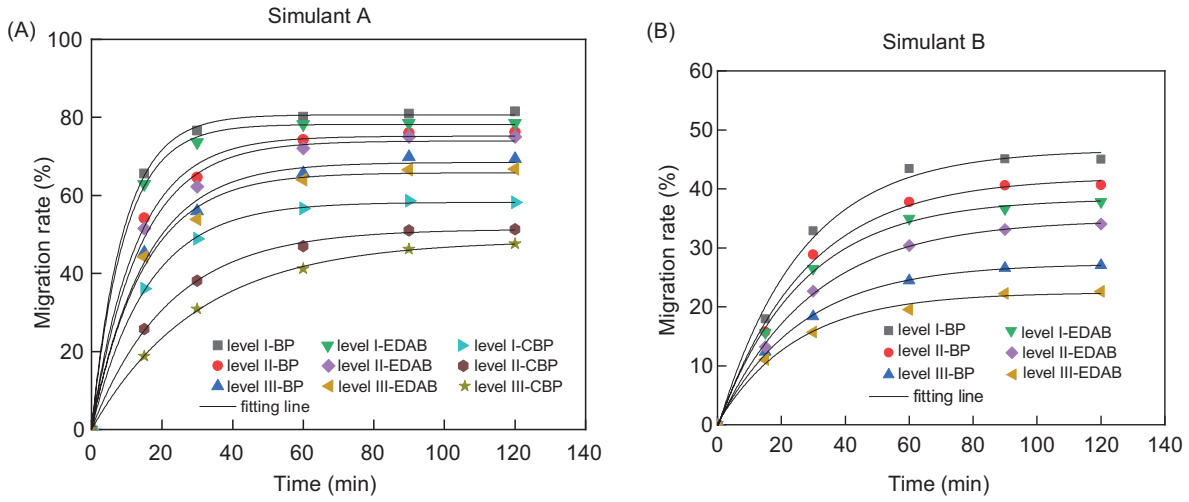

Figure 9. Fitting curves for the migration of the three photoinitiators into simulants A and B at different random vibration levels.

Table 5. Values for each parameter of the migration model.

Photoinitiators	Food simulants	RMS/g	$M_{F,\infty}$	A	b	R^2
BP	A	0.73	80.67	80.63	9.12	0.996
		0.52	75.20	74.86	12.80	0.996
		0.37	68.48	68.00	15.34	0.994
	B	0.73	45.26	45.26	26.33	0.997
		0.52	41.91	42.44	29.32	0.991
		0.37	37.31	37.20	30.62	0.996
EDAB	A	0.73	78.22	78.16	9.38	0.994
		0.52	73.97	73.56	13.82	0.995
		0.37	65.82	65.37	14.97	0.994
	B	0.73	38.34	38.61	24.54	0.996
		0.52	34.76	34.95	27.34	0.992
		0.37	32.43	32.19	28.22	0.996
CBP	A	0.73	58.27	58.16	15.91	0.997
		0.52	51.36	51.21	22.10	0.999
		0.37	48.46	48.45	30.24	0.997

BP, benzophenone; EDAB, ethyl 4-dimethylaminobenzoate; CBP, chlorobenzophenone.

No study in this area has been reported. In the future, the effect of other levels of random vibration or road-spectrum simulation vibration on the migration of harmful substances in PE-coated paper could be investigated.

BP's migration model.

$$\frac{M_{F,t}}{M_{F,\infty}} = (56.8 + 33.4ag) - (56.8 + 34.6ag) \times \exp\left[\frac{-t}{21.8 - 17.3 \times g}\right] \quad (5)$$

EDAB's migration model.

$$\frac{M_{F,t}}{M_{F,\infty}} = (54.6 + 33.4gg) - (53.7 + 34.6gg) \times \exp\left[\frac{-t}{21.3 - 15.9 \times g}\right] \quad (6)$$

CBP's migration model.

$$\frac{M_{F,t}}{M_{F,\infty}} = (37.8 + 27.6rg) - (37.8 + 27.6rg) \times \exp\left[\frac{-t}{43.9 - 39.1 \times g}\right] \quad (7)$$

Conclusion

In this study, we investigated the migration behavior of three PIs from PE-coated paper to acidic and neutral food simulants under different working conditions. Additionally, the effect of random vibration on the migration behavior of PIs was studied for the first time. The effects of temperature, microwave power, random vibration, migration time, and types of food on the PI migration rate under specific working conditions were also investigated by plotting the PI migration kinetic curves.

We found that the severity of the different working conditions led to an increase in the equilibrium migration rate of BP, EDAB, and CBP, which increased by approximately 10% at 100°C compared to 40°C. Compared with conventional heating, the migration equilibrium time of PI was shortened under microwave heating conditions. The equilibrium migration rate of BP, EDAB, and CBP was 10% higher under 800 W conditions than that under 400 W conditions. Under three different conditions, the mobility of three PIs increased with increasing temperature, microwave power, and random vibration acceleration by 10, 10, and 15%, respectively. Moreover, the migration rates of each PI into A were higher than those of B at the same migration time. The highest migration rates for BP, CBP, and EDAB were 81, 58, and 79%, respectively. In the same class of food simulants, the order of magnitude of the migration rate of the three PIs was BP > EDAB > CBP.

Finally, a mathematical model of the migration behavior of three PIs under different working conditions was developed and explained in terms of working principles and molecular properties, which can predict the migration of similar hazardous substances. Furthermore, the developed model can effectively predict the quality and safety of fast food packaging material, protecting the dietary safety of takeaway fast food consumers.

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