Migration of DEHP from plastic to food simulants under microwave heating

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Abstract. The migration of plasticizer DEHP from the plastic products (4 kinds of commonly used plastic food containers under microwave heating: plastic wrap, food bags, ordinary plastic boxes, microwave special plastic boxes) through food contact materials to food simulants (isooctane, 10% ethanol-water solution (*v/v*), 3% acetic acid-water solution (*w/w*) and distilled water) was studied under microwave heating (power levels of 400 W) .The results shows that the DEHP mobility increases with the increase of microwave heating time, DEHP mobility in isooctane and 3% acetic acid-water solution (*w/w*) is significantly greater than in 10% ethanol-water solution (*v/v*) and distilled water; the order of DEHP mobility in isooctane is plastic wrap>food bag>common plastic box>microwave-safe plastic box, while in 3% acetic acid (*w/w*), the order is food bag>common plastic box>microwave-safe plastic box>plastic wrap.

1. Introduction

DEHP is a typical one of Phthalate Esters (PAEs) which spread widely in the environment. It is often used as plasticizer of polyvinyl chloride plastics in industrial production [1]. DEHP has toxic effect on the reproductive system, respiratory system, heart and liver of animals, furthermore, clinical studies have found that DEHP also has physiological toxicities to human [2,3]. DEHP connects with plastic molecules by hydrogen bond or Van Edward force instead of firm covalent bonds, therefore, it's easy to enter the room, atmosphere, food, drinking water and other substances through ways of leaching, migration or evaporation [4].

Nowadays, microwave heating has become an important way of food cooking. Additionally, a certain group of people are forced to use plastic containers to keep and heat food by microwave for a long time because of fast pace of life. So food safety issues under the conditions of microwave heating have been paid more and more attentions [5-10]. At present, the study of migration under microwave heating is mainly focused on the migration from food packaging materials to food, while there is few researches about migration from food container plastic to food in such a short and extreme condition such as microwave heating [11-17].

In present study, 4 kinds of commonly used plastic food containers were selected to do a series of experiments under microwave heating, and isooctane, 10% ethanol-water solution (*v/v*), 3% acetic acid-water solution (*w/w*), distilled water were selected respectively as the fat simulants, wine

simulants, acid simulants, water simulants. Major objectives of the present study were to explore the influences of microwave heating time, plastic type, and food properties on migration rates of DEFP from plastic. Results obtained can provide reference for the safe use of food contact materials under microwave conditions.

2. Materials and methods

2.1. Material and reagents

4 kinds of commonly used plastic food containers were selected: New microwave plastic boxes made of polypropylene (PP); new ordinary plastic boxes made of polypropylene (PP); food special bags made of high density polyethylene (HDPE); food wrap films made of polyethylene (PE).
According to GB 23296.1-2009, SN/T 2037-2007 choose food simulants, as shown in Table 1.

Table 1. Food simulants.

type of simulants	food simulants
Aquatic food (pH>4.5)	distilled water
Acidic food(pH≤4.5)	3% acetic acid (*w/w*)
Alcohol food	10% ethanol (*v/v*)
Oily food	isooctane

2.2. Instruments and equipment

10% ethanol-water solution (*v/v*); 3% acetic acid-water solution(*w/w*); distilled water; isooctane(AR); methanol (GR); ethanol (AR); acetic acid (AR); hexane (AR); diethylhexyl phthalate (AR);

GC-4000A gas chromatograph; P70D20TJ-D3Galanz microwave oven; HH-2 thermostat water bath; DHG-9240AS electrothermal constant-temperature drying box; SB-300DTY ultrasonic cleaning machine; TG16-II centrifugal machines; EL204 electronic balance; ultrapure water filter (R＞18.2 MΩ).

2.3. Sample preparation

The plastic samples, which had been washed with aether and DI water in turn, were heated in microwave oven by submerging in food simulants. After microwave heating (power levels of 400 W), samples tested with isooctane were directly heated in water-bath, while samples tested with the three other food simulants need to be extracted by hexane and centrifugal separated firstly. When samples were heated in water bath to nearly dry, they were transferred into volumetric flask and constant-volumed.

2.4. Detection conditions

The GC-FID was chosen as the sample detection method for DEHP, and the chromatographic conditions were shown in Table 2.

Table 2. Working conditions of gas chromatography.

Detector type	Column model	Column temperature	Vaporization temperature	Hydrogen flame temperature
flame ionization detector (FID)	SE-54 capillary column	250℃	270℃	260℃
Protection temperature	Nitrogen pressure	Air pressure	Partial pressure of hydrogen	Sample volume
300℃	0.3MPa	0.2MPa	0.05MPa	1μl

2.5. Migration rate

The migration rate was calculated as follows:

$$R = \frac{S \times V}{a \times W}$$

Where, R is the migration rate of DEHP; S is peak area of sample (μV×s); V is the volume of sample after constant volume, here is 1 ml for all samples; a is the correlation coefficient of concentration and peak area, in this study, its 57791.35; W is the weight of plastic sample.

3. Results and discussion

3.1. Migration rates of DEHP to fat simulants

The change trend of DEHP mobility from different plastic food containers to fat simulants with microwave heating time was presented in Figure 1. For each kind of plastic container, migration rate of DEHP increased with the increase of microwave heating time, especially for food wrap films and food special bags. The migration rates of food wrap films and food special bags were obviously higher than that of microwave plastic boxes and ordinary plastic boxes. The migration rate of DEHP from food wrap films increased rapidly in the first 7 minutes, and then decreased.

The food wrap films and food special bags selected in this study are made of PE, while ordinary plastic boxes and microwave plastic boxes are made of PP. Usually plastic food containers made of PP or PE contain various levels of phthalic acid esters (PAEs) which can enhance the flexibility and ductility of plastics. DEHP is one of the most frequently used PAEs, which is added into most of the plastic products. The requirement of DEHP in PP is relatively lower than that in PE, which can explain the results aforementioned [18].

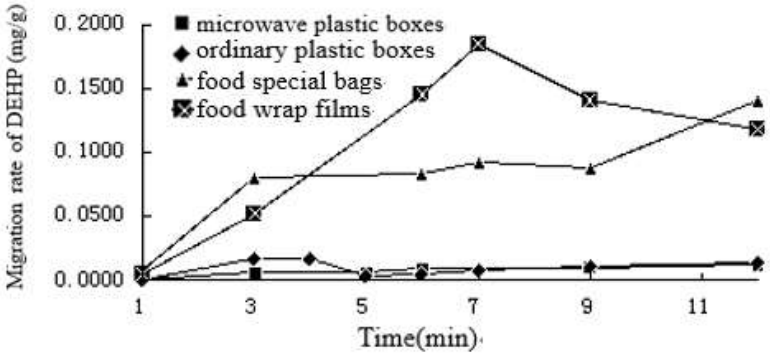

Figure 1. Migration rates of DEHP from different plastic food containers to fat simulants.

3.2. Migration rates of DEHP to acid simulants

The change trend of DEHP mobility from different plastic food containers to acid simulants with microwave heating time was presented in Figure 2. For each kind of plastic container, migration rate of DEHP increased with the increase of microwave heating time, especially for food special bags. The migration rates of food special bags were obviously higher than that of food wrap films, microwave plastic boxes and ordinary plastic boxes. Different with the migration regularity of DEHP to fat simulants, the migration rate from food wrap films to acid simulants remained stable until 6 minutes, and then increased in slow growth from 6 to 9 minutes while increased rapidly after 9 minutes.

Previous researches have shown that when ester groups of DEHP break down under the external conditions, they will combined with H+ or OH-. And the stronger the acidity or alkalinity of external conditions, the more favorable for the hydrolysis of DEHP, in other words, acidic conditions can promote the hydrolysis of DEHP to a certain extent [19]. At the same time, acidic conditions can accelerate the delamination and aging of the plastic products, resulting in decline of mechanical strength, to a certain extent, it can also promote the precipitation of DEHP [20]. Therefore, for the

three kinds of non-oily food simulants (wine simulants, acid simulants and water simulants), the migration rate of DEHP from acid simulants is higher than the other two.

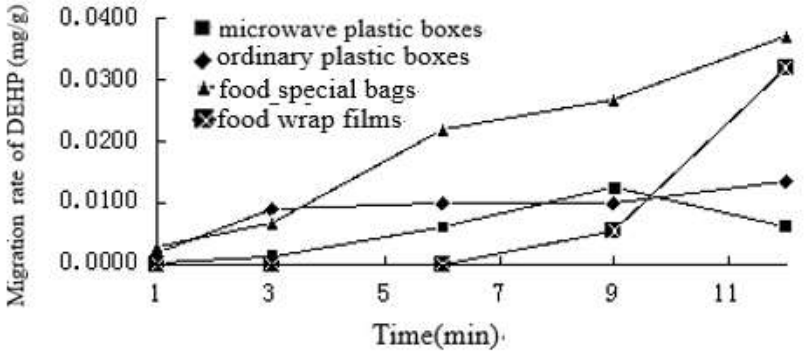

Figure 2. Migration rates of DEHP from different plastic food containers to acid simulants.

3.3. Migration rates of DEHP to wine simulants

The change trend of DEHP mobility from different plastic food containers to wine simulants with microwave heating time was presented in Table 3. Similarly, for each kind of plastic container, migration rate of DEHP increased with the increase of microwave heating time. However, due to the low migration rate of DEHP to wine simulants, the increasing trend was not obvious. In general, the migration rate of food special bags was slightly larger than that of the other three plastics.

Table 3. Migration rates of different kinds of plastic food containers to wine simulants (mg/g).

Heating time	microwave plastic boxes	ordinary plastic boxes	food special bags	food wrap films
1min	0.0016	---	0.0032	---
3min	---	0.0003	0.0051	0.0014
6min	0.0006	0.0023	0.0024	0.0024

3.4. Migration rates of DEHP to water simulants

The change trend of DEHP mobility from different plastic food containers to water simulants with microwave heating time was presented in Table 4. DEHP is the lipophilic organic compounds, so it's molecular structure is quite different from that of H_2O. According to the theory of similar dissolve mutually, the solubility of DEHP in water is very poor. As shown in Table 3, overall the migration rate of DEHP from the plastic to water simulants is fairly low, therefore, there is no significant change trend of migration rates.

Table 4. Migration rates of different kinds of plastic food containers to water simulants (mg/g).

Heating time	microwave plastic boxes	ordinary plastic boxes	food special bags	food wrap films
3min	---	---	---	0.0032
6min	0.0024	0.0016	0.0022	---
9min	---	0.0009	---	0.0046

3.5. Migration rates of DEHP to different food simulants under the same heating time

Heating time of 3 and 6 minutes were selected to investigate the variation laws of migration rate with time, as shown in Figure 3 and Figure 4. The results indicated that basically the migration rate of DEHP with 6 minutes heating time was higher than that of 3 minutes; the migration rate of DEHP to fat simulants was significantly higher than the other three food simulants. DEHP is a moderately low

polar compound and easily soluble in solvents with similar polarity such as isooctane, so DEHP in plastic is more likely to migrate to fat simulants (isooctane). Under the condition of non-microwave heating, the regularity also exists. For example, when the food-grade plastic inner materials was soaked in the four kinds of food simulants for 6 days under 60℃, respectively, the migration rate of DEHP to fat simulants was the biggest, which can reach 22% [21].

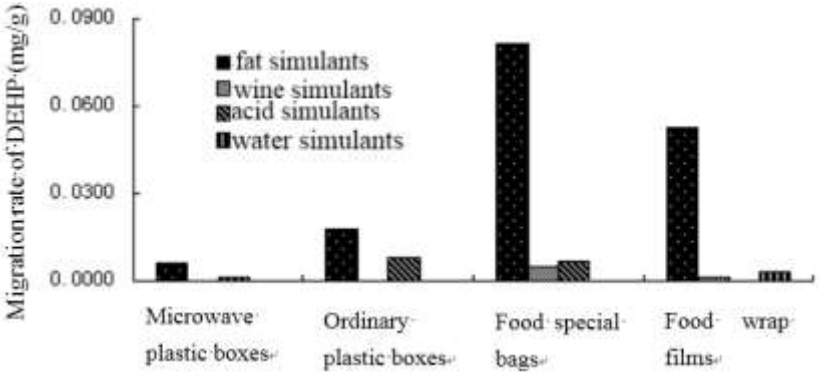

Figure 3. Migration rates of DEHP from different plastic food containers to simulants when heating time is 3 minutes.

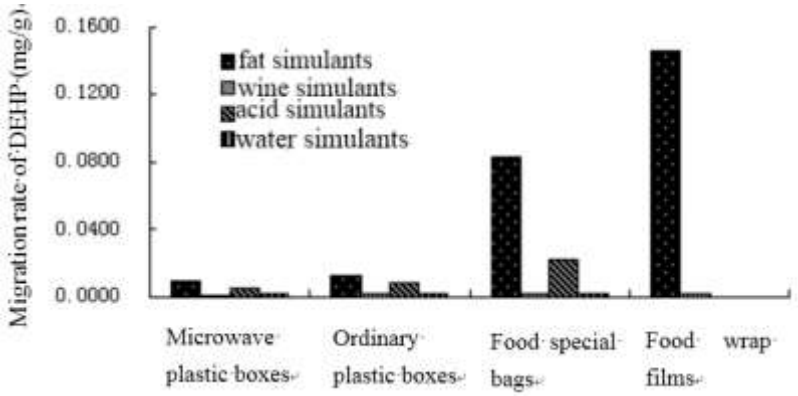

Figure 4. Migration rates of DEHP from different plastic food containers to simulants when heating time is 6 minutes.

4. Conclusions

With the increase of microwave heating time, the migration rate of DEHP in the four kinds of plastic food containers increased in varying degrees, that is, the migration rate of DEHP was positively correlated with the microwave heating time. The migration rate of DEHP to fat simulants was the largest, and was the smallest in water simulants. In addition, DEHP migration rate of all kinds of plastic food containers except food wrap films, was second in acid simulants behind fat simulants.

Moreover, DEHP migration rates of different plastic food containers had the similar regular which decreased in the order of following order: food special bags>ordinary plastic boxes>microwave plastic boxes; Only the migration rate in food wrap films was unique, as the results aforementioned indicated, for food wrap films, the migration rate to fat simulants was the biggest in the four kinds of plastic food containers while that of acid simulants was the lowest.

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