Research Article
Antioxidant BHT Modelling Migration from Food Packaging of High Density Polyethylene Plastics into the Food Simulant

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Abstract: Made of High Density Polyethylene (HDPE) films containing antioxidant 2, 6-di-tert-butyl-p-cresol (BHT), film samples were manufactured by plastic extrusion equipment, 95% ethanol aqueous solution simulating liquid was used for stimulant, using High Performance Liquid Chromatography (HPLC) for the long-term migration test of 4 kinds of HDPE films containing different concentrations of antioxidant BHT. The migration data were processed by using Weibull model and then the migration model was specific under experimental conditions. Migration model was setup using the migrating data by Weibull model to fitting real experimental data. Using empirical formula reported FDA model formula and the diffusion coefficient constant D, calculated by the FDA model. Two kinds of model numerical after compared according to FDA model transfer numerical literature that is far lower than the actual test migration value. According to the actual test migration value, Weibull model numerical and experimental tests that the migration software fitting values are consistent.

Keywords: Antioxidant, high density polyethylene, migration, model

INTRODUCTION

High Density Polyethylene (HDPE) is a general purpose plastic, widely used in food packaging material and food containers, HDPE plastic will degradation in processing and long-term used conditions, therefore which must to add antioxidants in the process of processing to ensure the plastic properties. If antioxidants was migrating to the food and migrating into the body may cause damage to health. (2, 6-di-tert-butyl-p-cresol) (BHT) belongs to the commonly hindered phenolic antioxidants used in the food packaging materials.

Many kinds of additives were added into food packaging plastic, the same plastic may add several additives, so the migration test workload associated with the establishment of the great migration, the corresponding mathematical model and experimental data, the experimental workload can be reduced and can simplify the research, migration model can also be used for theoretical analysis and risk forecast, which can use to food safety monitoring and guidance of food packaging materials (Gillet *et al.*, 2009). The purposes of this study is to test the antioxidant BHT of HDPE migration by High Performance Liquid Chromatography (HPLC) and then study the migration model and set up the model based on the test data.

High Density Polyethylene (HDPE) is a kind of general purpose plastics, widely used in food packaging material and food containers, HDPE plastic conditions prone to aging degradation is used in processing the material properties and long-term decline, affect the use, therefore must to join some antioxidants to ensure the plastic properties. If the antioxidants migrate to the food, with the food into the human body may cause damage to health. (2, 6-di-tert-butyl-p-cresol) (BHT) belongs to the commonly used in the food packaging materials of hindered phenolic antioxidant. Food packaging plastic contained many kinds of additives, the same plastic may add several additives, so the corresponding mathematical model with migration test workload associated with the establishment of the great migration, can reduce the experimental data and experimental workload and can simplify the study, migration model can also be used for theoretical analysis and risk forecast, has important meaning to the use of food safety monitoring and guidance of food packaging plastics. To test the antioxidant BHT of high density polyethylene migration by High Performance Liquid Chromatography (HPLC), then study the migration model.

Study on mathematical model of existing additives migration in food packaging plastic is mainly based on the description of the Fick's second law of non-steady

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molecular diffusion, Piringer (Baner *et al.*, 1996) got Eq. (1):

$$\frac{M_{F,t}}{M_{F,\infty}} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp[-D \bullet t \frac{(2n+1)^2 \pi^2}{L^2}] \quad (1)$$

where,

$M_{F,t}$: The quality of migrant in the stimulant
$M_{F,\infty}$: The quality when at the equilibrium
D : The diffusion coefficient
L : The thickness of the material

Equation (1) in the complete migration or migration time shorter assumptions, got a simple Eq. (2), called the FDA model (O'Brien *et al.*, 1999; Limm and Hollifield, 1996):

$$\frac{M_{F,t}}{M_{F,\infty}} = \frac{2}{L\sqrt{\pi}} \sqrt{D t} \quad (2)$$

The Weibull model is put forward in the study of Swiss mathematician Waloddi Weibull bearing reliability, has been widely used in various research fields. Weibull model is a mathematical model based on the probability and mathematical statistics methods. Its parameters are not given the actual physical meaning, so when in use restrictions rarely, can direct the experimental results are explained and characterization does not consider process and constraints of chemical experiment occurred, it is characterized by a few parameters, simple computation and strong applicability, which was a wide range of applications.

The formula of Weibull model as Eq. (3) (Poças *et al.*, 2012):

$$\frac{M_{F,t} - M_{F,\infty}}{M_{F,0} - M_{F,\infty}} = \exp[-(\frac{t}{\tau})^{\beta}] \quad (3)$$

where,

$M_{F,0}$: The quality migrant of initial time in the stimulant
τ : System parameters
β : Shape parameters (Poças *et al.*, 2012)

Study on the migration of existing models mainly focus on the Fick's second law model, focus on the important parameters. Begley *et al.* (2005) studied the antioxidants in PP migration using Piringer migration model, the various parameters of antioxidants in the values of the model were solved, but the simulated liquid single species not comprehensive, antioxidant. Reinas *et al.* (2012) using the FDA model study two antioxidants of Irgafos 168 and Irganox 1076 in Low Density Polyethylene (LDPE) migration research, found that the FDA model can be used for solid simulation of migration prediction in good. Poças *et al.* (2012) collected the data of PP, LDPE, migration from 4 laboratory studies, conducted by Weibull model

analysis of antioxidants migration in HDPE and concluded that Weibull model can be used to study the migration of additives in food packaging plastic. But based on the High Density Polyethylene (HDPE), antioxidant BHT migration in the material, applicability and comparison of Weibull model and FDA model has not been reported in literature, this study will research.

In this study, experimental process was made of a series of HDPE films for simulation studies, by adding different mass percent of antioxidant BHT, made HDPE film samples with different concentrations. The samples were then soaked into simulated solution for migration experiments, using HPLC to test different time points in the final analysis concentrations migration solution, using the software fitting data modeling.

MATERIALS AND METHODS

Reagent and instrument: PolyLab OS (Thermo, USA); Panel vulcanizer (Xihua testing machine Co., Ltd.); HPLC (LC-20A and SPD-M20A Array Detector (DAD), Shimadzu, Japan) 2, 6-di-tert-butyl-p-cresol (BHT) (99.0%, Sigma-Aldrich Co.); Acetonitrile (HPLC Grade): Fisher Scientific; Ethyl alcohol absolute (HPLC Grade): J.T Baker. HDPE resin (Beijing Yanshan Petrochemical Co.)

The sample preparation: The sample making process is adding antioxidant BHT powder into certain proportion of HDPE resin, through HAAKE PolyLab OS on 190°C granulation by double screw plastic extruder. Then weigh a certain amount of master batch, through flat vulcanizing machine 190°C hot pressing film (0.1 mm). Sample informations of BHT content are shown in Table 1.

Method of BHT test: The HPLC conditions for the flow rate: 1 mL/min, column temperature: 45°C, the A of the mobile phase acetonitrile mobile phase, B for water. Gradient elution: 0-5 min A, 75%; 5-20 min A, 100%; 20-25 min, 100% 25-30 min, 75% A. sample volume: 20 μL, detection wavelength: 282 nm. Column: C18 (250*4.6 mm*5 μL, Phenomenex Co. American).

The chromatogram of BHT as shown in Fig. 1. Quantitative determination of antioxidants by external standard method.

Method of migration testing: The sample films experiment selected 4 type films as Table 1, which were cut into 3*4 cm rectangular (total areas 24 cm^2), each sample of 2 parallel samples were placed in 60 mL screw cap glass bottle, add 40 mL liquid stimulant and immersion sample film. The glass bottle is placed in the

Table 1: Sample information

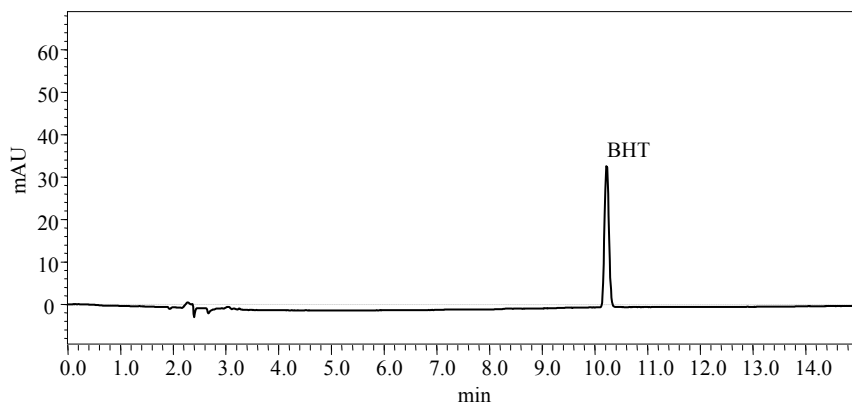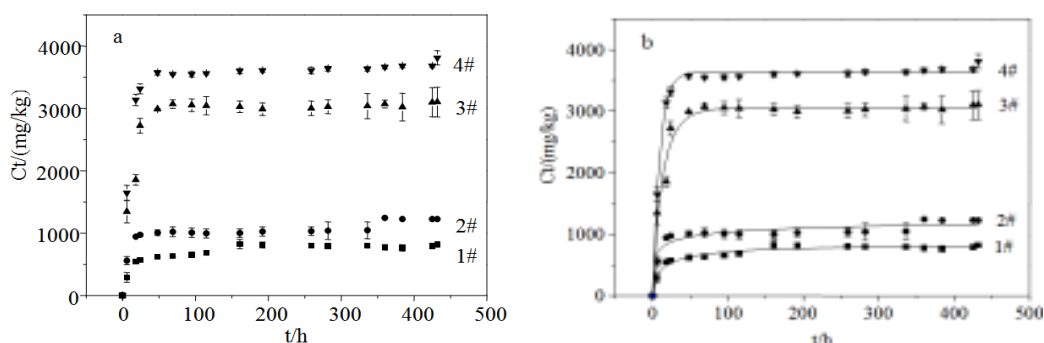| Sample No.	BHT con. (g/kg)
1#	1.25
2#	2.00
3#	6.00
4#	8.00

Fig. 1: Antioxidant BHT chromatogram

Fig. 2: The migration curve of BHT; (a): Experimental data (■: 1#; ●: 2#; ▲: 3#; ▼: 4#); (b): The Weibull model fitting (■: 1#; ●: 2#; ▲: 3#; ▼: 4#)

oven (temperature of 40°C) heating. At intervals of 20 μL out trace simulation of liquid on the antioxidant BHT, which were quantitatively test by HPLC.

RESULTS AND DISCUSSION

Migration pretreatment method selection: Study on the migration of HDPE food contact materials in food simulants, used to replace the real food to simulate the migration process. B provisions of selected 95% ethanol aqueous solution as lipid food simulants (EN13130-1, 2004). Plastic surface area is 6 dm^2 in 1 L (simulation of liquid food, all food density can be assumed to be 1 kg/L). At the same time the provisions of migration experiment can be adjusted by the appropriate area to volume ratio of the experimental concentration to obtain the ideal. For symmetric, homogeneous samples, can be full immersion migration test. In this study the migration pre-processing steps as shown in 2.4, migration temperature selected 40°C as temperature of migration.

Comparison research of two migration models: European standard (EN13130-2, 2004), B rules in some cases the result of migration can be used to represent the mass ratio (mg/kg), for the convenience of the study and to minimize the error between samples, defined in the migration of the same area. $C_t = M_{F,t}/M_P$, The unit is

mg/kg, M_p: the quality of food packaging materials. $C_{F,0}$: In the initial stage of migration can be considered for simulation of liquid antioxidant content was 0, take it into the Eq. (3) got the Eq. (4):

$$C_t = C_{F,\infty} - C_{F,\infty} \bullet \exp[-(\frac{t}{\tau})^{\beta}]$$ (4)

We take $C_t = M_{F,t}/M_P$ into the Eq. (2) can be get the Eq. (5):

$$\frac{C_t}{C_{F,\infty}} = \frac{2}{L\sqrt{\pi}}\sqrt{Dt}$$ (5)

Using the HPLC test at different time points of BHT concentration in food simulants, with time as the abscissa, taking Ct as the ordinate, do the migration of data scatter diagram as shown in Fig. 2a, followed by a nonlinear fitting function in Origin software, set of unknown parameters fitting for τ, β, C∞, the numerical experiments for the Ct approach Eq. (4), fitting a Weibull model of nonlinear fitting curve as shown in Fig. 2b and obtained 4 samples of different concentrations of Weibull model parameters are shown in Table 2.

The most important parameters of the FDA model is the D, there are lots of experience formula of its value, the Brandsch formula is widely used, which is

Table 2: Weibull model fitting parameters

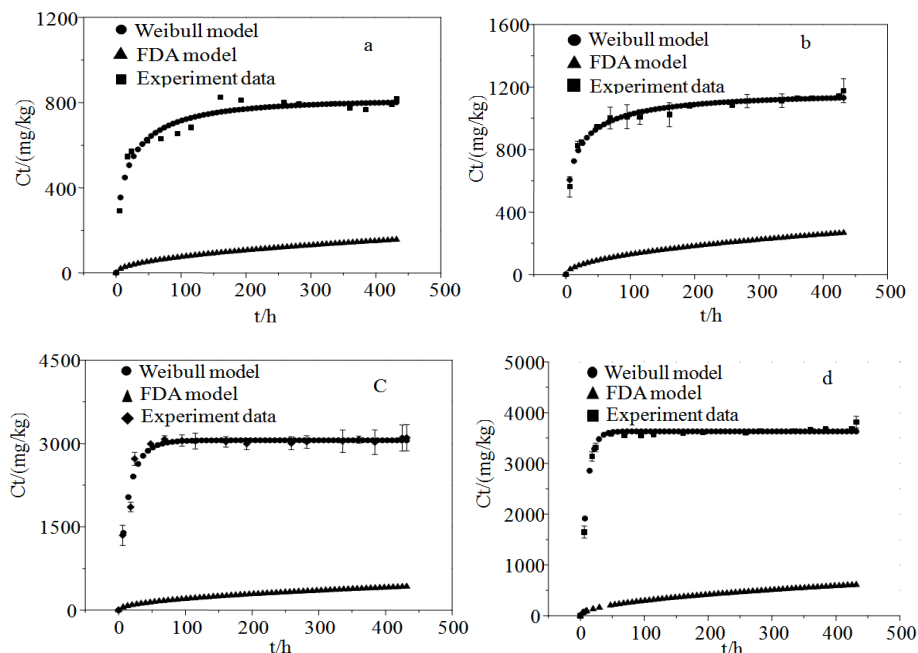| C_{P0} (mg/kg)	τ (h)	β	$C_{F,\infty}$ (mg/kg)	R^2
1250	21.20	0.486	811	0.970
2000	12.10	0.280	1242	0.922
6000	13.20	0.850	3056	0.979
8000	9.65	1.040	3629	0.996

Fig. 3: Comparison of Weibull model and FDA model; (a): 1#; (b): 2#; (c): 3#; (d): 4# (●: Weibull model; ▲: FDA model; ■: Experiment data)

shown in Eq. (6) (Baner *et al.*, 1996; Begley *et al.*, 2005):

$$D = 10^4 \exp(A_P - 0.1351M^{2/3} + 0.003M - 10454/T) \quad (6)$$

where,

M : Molecular weight of the migration of additives in food packaging materials

T : Temperature $A_P = \acute{A}_p - τ/T$

The value of the parameter D in FDA model, using the empirical Eq. (6) can be computed, which Piringer migration experiment analysis and collection of literature then draw the conclusion and Ap values of material such as HDPE, experience value is 1577, Ap' experience value is 14.5, the empirical formula in the concentration of migration is less than 1% and transfer temperature of less than 100°C under the premise of the establishment (Reinas *et al.*, 2012). Using Eq. (6) calculated the data obtained the various constants at 40°C, BHT diffusion coefficient D was 5.65E-09 in HDPE plastics, take D value into FDA model Eq. (5), in order to facilitate comparisons and Weibull model data, Eq. (5) in C_F, infinity from Table 2 value, the equations of the calculated under different time of migration of BHT numerical curve. The parameters of Weibull model according to Table 2 into the model the

Eq. (4), obtains the different migration time migration under BHT value curve. FDA model and Weibull model migration migration curve as shown in Fig. 3.

Weibull migration model establishment: The FDA model has the characteristics of simple calculation, less parameters. Combined with the Eq. (4) the D value of the empirical formula calculation can be very convenient to the valuation, the migration of simple plastic antioxidants PE and PP values in the prediction, but the FDA model is simplified to a model, while the value of D according to the literature experience formula, for different food simulants D value no refinement, errors existed in the valuation of real samples in the prediction of. As from Fig. 3, the predicted migration value using the FDA model, the numerical prediction to migrate far below the actual value. According to the measured values obtained by fitting the Weibull model software migration numerical and experimentally determined values are consistent.

In the Weibull model the migration speed depends on the τ parameters. Therefore, τ parameter can be used as a characterization of migration rate. In the chemical reaction kinetics, there is Arrhenius relationship between rate constant and temperature:

$$k = A*\exp(-E/RT) \quad (7)$$

Therefore the establishment of τ correlations with temperature by Eq. (8):

$$\frac{1}{\tau} = A\exp(-\frac{E}{RT}) \tag{8}$$

Plasticized by cohesive agent migration can be defined in PVC, the density of CED, CED = E/V and defined the solubility parameter δ^2 = CED, there is defined formula δ^2 = E/V, E: the Activation energy, unit is J/mol, V can be used to characterize the molar volume, unit is cm^3/mol. We can get Eq. (9) and (10) use parameters above:

$$\tau = \tau_0 \exp(\frac{\delta^2 M_w}{\rho RT}) \tag{9}$$

where,
τ_0: Constant
E: Activation energy
T: Kelvin T:

$$\frac{C_t}{C_\infty} = 1 - \exp\left[-\left(\frac{t}{\tau_0 \exp(\frac{\delta^2 M_w}{\rho RT})}\right)^\beta\right] \tag{10}$$

where,
δ : The solubility parameter
M_W : The molecular weight of BHT
T : The temperature of migration
ρ : The density of BHT
$C_{p,0}$: The content of BHT in sample

CONCLUSION

The HDPE film samples were made by plastic extrusion equipment, the mass percentage concentration of antioxidant BHT is added into the 4 HDPE samples concentration of 0.125, 0.2, 0.6 and 0.8%, respectively as a lipid migration solution made a long migration test using 95% ethanol aqueous solution, migration of BHT in the liquid simulation was rapid. Using the Weibull model to fit the experimental data obtained Weibull migration model under the experimental conditions. Using the empirical formula of FDA model that reported in the literature and got the constant D which calculated by the FDA numerical model under the

conditions. Comparison of two kinds of model, found according to FDA migration model data is far lower than the actual value of the test data. While the Weibull model data and experimental data are fitting, then the model was established.

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