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EVALUATION OF LOSS OF 2-TERTIARY
BUTYL-4-METHOXY PHENOL (BHA) FROM HIGH
DENSITY POLYETHYLENE FILM
presented by
JONG KOO HAN

has been accepted towards fulfillment
of the requirements for
M. S. degree in PACKAGING

Drs. Bruce Harte & Jack Giacin
Major professors

Date November 8, 1984

Handwritten signatures of Bruce Harte and Jack R. Giacin in black ink.

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EVALUATION OF LOSS OF 2-TERTIARY BUTYL-4-METHOXY
PHENOL (BHA) FROM HIGH DENSITY POLYETHYLENE FILM

By

Jong Koo Han

A THESIS

Submitted to

Michigan State University

in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

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ABSTRACT

EVALUATION OF LOSS OF 2-TERTIARY BUTYL-4-METHOXY PHENOL (BHA) FROM HIGH DENSITY POLYETHYLENE FILM

By

Jong Koo Han

Loss of the antioxidant, 2-tertiary butyl-4-methoxy phenol (Butylated Hydroxy Anisole; BHA), from food grade high density polyethylene (HDPE) film was measured over the range of 10-50°C.

To determine the loss of BHA from the HDPE film, the BHA content of the film sample was measured at pre-determined time intervals by a high pressure (performance) liquid chromatography (HPLC) method.

The kinetic curves of loss of BHA from the film followed a first order relation over the range of temperatures studied, i.e. 10-50°C. The rate constants and the activation energy were calculated from the rate of loss.

The diffusion coefficient of BHA in HDPE film and the mass transfer coefficient of BHA from HDPE film to air were estimated by an analytical model that assumed the loss rate controlling resistance was the rate of evaporation of BHA from film to air. The experimental loss-time data were well correlated by the analytical model.

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INTRODUCTION

Polyethylene is the most produced synthetic packaging material in the world. The total polyethylene film production in the U.S.A. was estimated to be in excess of 2.3 billion lbs.. in 1980, of which more than 50% was used in food packaging (Rich, 1982).

Polyolefins, such as polyethylene, are subject to thermal and oxidative degradation. During the processing of polymers at high temperatures (i.e. 200-300°C) and/or their subsequent exposure to the environment in the presence of oxygen, free-radical chain reactions can take place, leading to scission and crosslinking of the polymer chains and consequently to deterioration of the physical properties of the polymer.

The resistance of polymeric materials such as polyethylene toward thermal and oxidative degradation can be enhanced by the incorporation of antioxidants, mainly sterically hindered phenols, into the polymer during processing. 2-Tertiary butyl-4-methoxy phenol (BHA) is one of the most widely used antioxidants in the production of polyethylene film.

However, antioxidants, such as BHA which inhibit the degradation of polyethylene, eventually fail to give

adequate protection, and rapid degradation of the polymer occurs (Hawkins et al., 1960). Antioxidants present in the polymer can be subject to chemical reactions (i.e. oxidation) leading to the formation of complex mixtures of thermal and photochemical reaction products derived from the antioxidant. There are several other factors which may contribute to antioxidant failure. One of the factors which determines the efficiency of phenolic antioxidants is the loss by evaporation from the polymer surface.

An understanding of the transfer mechanism(s) of BHA from packaging film to product would make it possible to better design and select packaging systems for controlled transfer of BHA. This study examines the loss rate of BHA from high density polyethylene film at several temperatures. Additionally, simulation models were employed to identify the loss mechanism of BHA from the film. Calculated loss times using these models were compared with the experimental loss-time data.

The primary objectives of this study were: 1) to determine the mode of loss of BHA from high density polyethylene film as a function of temperature, and 2) to determine the diffusion coefficient of BHA in HDPE and the mass transfer coefficient from the film's surface.

LITERATURE REVIEW

Antioxidants of several types are commonly incorporated into polymers at concentrations of 0.01 to 1.0% (W/W) to minimize the effects of oxidative degradation, both during processing and in the subsequent service life of the polymer. Although many antioxidants are available, BHA is one of the most widely used additives in the production of polyethylene film. Further, BHA is generally recognized as safe for addition to food products. Food products covered by the Food, Drug and Cosmetic Act are allowed to contain a total of 0.02% of BHA based upon the fat content of the food, while food products covered under the Meat Inspection Act and the Poultry Inspection Act generally can be treated with up to 0.01% of an individual antioxidant and a combined total of not more than 0.02% of all approved antioxidants based upon the weight of the fat (Stuckey, 1972). It has been estimated that man consumes less than 0.1 mg/kg body weight daily of BHA (Johnson, 1971; Collings and Staratt, 1970). At levels 500 times this amount (50 mg/kg/day), BHA appears to be free of any obviously injurious effects. But, at larger doses (500 mg/kg/day), BHA results in certain pathological,

enzyme, and lipid alternations in both rodents and monkeys (Brannen, 1975).

For medical and food packaging applications, migration is a problem of major concern in packaging and especially in the selection and use of plastics packaging materials. BHA in polyethylene film can migrate to a contact phase (i.e. food stuff). Complex mixtures of thermal and photochemical reaction products derived from BHA are also subject to migration. Although numerous oxidation products have been isolated and identified from the oxidation of 3,5-ditertiary butyl-4-hydroxy toluene (BHT) with a variety of oxidizing agents (Aoki, 1962), it has only been recently that oxidation products of BHT present in polyethylene packaging materials have been isolated and characterized (Daun et al., 1974; Lichtenthaler and Ranfelt, 1978). Few attempts have been made to isolate and identify the oxidation products of BHA.

Analysis of these additives and their transformation products has become increasingly urgent in routine control and particularly in connection with food and drug packaging, where identities and levels of potentially toxic substances must be accurately known and controlled. The difficulties in determining and identifying antioxidants arise from three factors (Wheeler, 1968); namely: (1) high reactivity and low stability of antioxidants; (2) the low concentrations (0.1-1%) at which

they are present; and (3) the relatively insoluble polymer matrix. Therefore, isolation of the additives from the polymer, careful handling of the extracts and short analysis times are required if quantitative results are to be obtained. Wyatt and Sherwin (1979) used direct sampling gas chromatography to measure the loss of BHA from polyethylene. Howard (1971) and Pospisil et al. (1972) have shown how useful gel permeation chromatography can be for the analysis of polymer additive systems. A shorter analysis time was obtained by Majors (1970) and by Wims and Swarin (1975) by using liquid adsorption chromatography.

Antioxidants incorporated in plastics usually fulfill two important roles: a) protection during processing, often under conditions of extreme thermal stress (temperature above 200°C); and b) they protect plastics during use, especially where they are exposed to elevated temperature and unusual atmospheric conditions. To ensure processing and long-term stability, the polymers are protected by antioxidants, mainly sterically hindered phenols.

The ability of any additive to stabilize a polymer against thermal or photochemical effects depends mainly upon its interference with the chemistry of the oxidation process. However, an important secondary factor is that the additive must be retained in the polymer long enough

for its stabilizing potential to be effective. It has been recognized that the loss of additives by volatilization from the polymer surface may be a very important factor in determining service life. However, in view of the complexity of experimental determination of this characteristic, the amount of information in the literature is very limited. Hawkins et al. (1960), Temchin et al. (1970), and Bair (1973) have shown that typical stabilizing additives are lost from polyethylene films, both above and below the melting point of the polymer, at rates which are significant relative to the life time of the polymer.

Additives are invariably put into polymers by melt processing, where they are likely to be completely soluble. Assuming that a compatible additive can loosely be defined as a system which can be put into the polymer in a form in which it is effective and which will remain in the polymer long enough to be able to exert its stabilizing effect, then it is useful to examine the factors that are important in determining additive loss. Assuming that an additive is completely soluble and present in the polymer as a homogeneous solution, the rate of loss of additive is determined by two factors (Angert et al., 1961). The loss rate is determined by the rate of volatilization of additive from the polymer surface, which will act to create a concentration gradient

at the surface. Subsequently, material depleted from the surface must be replaced by diffusion from the bulk so that the overall loss process depends upon both the rate of evaporation across the polymer surface and the rate of diffusion within the polymer.

By comparison of theoretical and experimental data, Angert et al. (1961) concluded that the loss of phenyl- β -naphthylamine from thick rubber samples was dominated by the rate of removal of the additive from the surface, although they did not correlate this rate with the additives volatility.

Unfortunately, despite this early work, subsequent investigators have largely considered compatibility in terms of only one of these important factors.

As part of a study of additive migration, Westlake and Johnson (1975) examined the extraction of 2,4-dihydroxy-benzophenone from thin films of polymer into water and Till et al. (1982) studied the migration of 3,5-ditertiary butyl-4-hydroxy toluene (BHT) from high density polyethylene film to foods and food simulants. Results were presented in terms of a diffusion coefficient model. Similarly, Cicchetti et al. (1968) proposed that diffusion was the most important property of an anti-oxidant.

In contrast, most other authors have attempted to consider antioxidant loss in terms of volatilization,

ignoring the role of diffusion.

Durmis et al. (1975, 1976) correlated antioxidant loss from slabs of polypropylene with measurements of bulk volatility. Similar correlations have been attempted for polyolefins by other authors (Schmitt and Hirt, 1960).

In view of the lack of any quantitative model to describe the loss of additives and the importance of the problem in industrial practice, especially for polymeric packaging materials, an attempt was made to develop a model which could take into account the involvement of diffusion and evaporation in the loss of BHA from HDPE.

A quantitative model describing the loss of an additive such as the antioxidant, BHA, from a polymer film would have considerable practical importance in estimating the time to sample failure, as well as for cases where product shelf-life is related to the transfer of antioxidant from the package surface to the package internal environment and subsequently sorption onto the product surface.

Calvert and Billingham (1979) had pointed out that the loss of a simple low molecular weight additive such as 3,5-ditertiary butyl-4-hydroxy toluene (BHT) from thick films and bulk solid is determined by diffusion, while loss from thin films is controlled by the evaporation rate of the additive. In this study, thin film

samples and a simple low molecular weight additive, i.e. BHA, were used. It was assumed, therefore, that the loss rate controlling resistance was the rate of evaporation of BHA from film to air.

In addition, a complete model would also need to take into account the consumption of additives by oxidation and ultraviolet light effects. For the present both of these factors are neglected since they excessively increase the complexity of the model.

EXPERIMENTAL

Film Sample

The high density polyethylene film (HDPE) used for sample preparation was CROWN ZEELON 405 B (density: 0.954 g/cm^3), obtained from the Crown Zellerbach Film Production Division. The HDPE film contained 0.14% (w/w) BHA which was pre-mixed by the film manufacturer. The film was received as roll stock whose total weight was 10 lbs (2 mils thick x 12" wide). The film was stored at a temperature of 10°C .

Film Sample Preparation

Film samples were cut from the roll to give a total weight of at least 5 g (approximately 12" x 18"). Two sheets were cut for each test condition to provide for duplicate runs. Before the film samples were cut, several plies of the film roll were removed and discarded to prevent the possible evaporation of BHA from the outer surface of the roll of film.

The film samples were stored in constant temperature chambers maintained at 30°C , 40°C , and $50 \pm 1^{\circ}\text{C}$ respectively, as well as in a temperature controlled room maintained at $22 \pm 1^{\circ}\text{C}$, and in a refrigerated chamber at $10 \pm 1^{\circ}\text{C}$. The

time intervals between sample analysis for each temperature were determined by preliminary examination.

Film samples were mounted on a frame to prevent contact between samples. Film samples were clipped to the frame with pins or adhesive tape. Loss of BHA occurred from both surfaces of the film sample. Care was taken to insure the film samples were shielded from light.

Extraction Procedure

Film samples (5 g) were cut into small pieces and extracted with 150 ml of acetonitrile in a Soxhlet extraction apparatus for 12 hours. The extracts were then filtered. After extraction, losses of solvent by evaporation were adjusted by adding acetonitrile to a total volume of 200 ml.

Chromatographic Apparatus

Analysis of BHA was carried out by a high pressure liquid chromatography (HPLC) procedure. The HPLC system consisted of a Perkin Elmer Series 3B Solvent Delivery System and a LC-1000 Column Oven with a Perkin Elmer LC-85 Spectrophotometric Detector. The detector was interfaced to a Spectra Physics SP4200 Computing Integrator for quantitation. The chromatographic conditions were as follows:

Column; a 0.26 x 25 cm ODS-HC sil-x-1 stainless steel
(Perkin Elmer)

Solvent system; 60% Acetonitrile/40% distilled water
(v/v)

Flow rate; 1 ml/min.

Detector wavelength; 291 nm

Injector; 10 μ l Hamilton Microliter #701-N Syringe

Peak areas and retention times were determined by the computing integrator. The concentration of BHA in the film sample was determined from standard graphs constructed by analyzing pure BHA samples in acetonitrile.

Figure 1 shows a typical chromatogram of the extract from a HDPE-BHA sample. The BHA peak eluted at a retention time of about 1.9 minutes.

Calculation of Loss Rate and the Activation Energy

Kinetic curves of loss of BHA from the HDPE film followed a first order relationship. On a semi-logarithmic scale ($\ln C/C_0$ vs. time), the loss-time data showed a straight line relationship. A first order reaction is one in which the rate of the reaction is proportional to the concentration of only one of the reacting substances (Benson, 1960).

Algebraically

$$\frac{dc}{dt} = -kC$$

1)

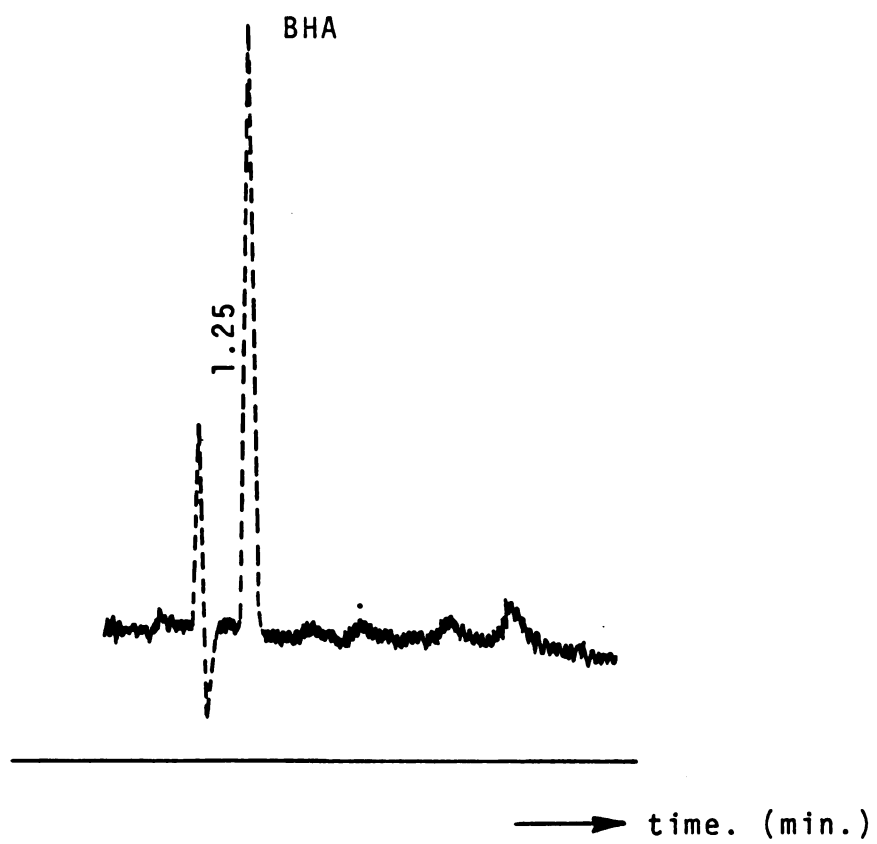


Figure 1. Typical chromatogram of extract from HDPE-BHA sample.

which can be integrated to give

$$\ln C/Co = -kt \quad 2)$$

where: Co, C = Initial and final concentration of BHA
in the film sample, % (w/w) respectively

k = rate constant, 1/hr

t = time interval, hr

The activation energy, the influence of temperature on the loss rate, was calculated from the differential form of the Arrhenius equation.

$$\ln \frac{k_1}{k_2} = \frac{Ea}{R} \left(\frac{T_1 T_2}{T_1 - T_2} \right) \quad 3)$$

where: k_1, k_2 = rate constant at each temperature

T_1, T_2 ; 1/hr

T_1, T_2 = temperature, $^{\circ}K$

Ea = activation energy, cal/mole

R = gas constant, 1.987 cal/ $^{\circ}K$.mole

RESULTS

Experiments were carried out according to the previously described procedures. Each concentration value is the average of four separate chromatographic analysis of the extractant phase.

The results of the studies carried out over the temperature range of 10-50°C are tabulated in Table 1 to 5, respectively. For better illustration, the results are presented graphically in Figure 2, where the relative percent BHA present in the test film is plotted as a function of time. The loss of BHA from the HDPE films, as shown in Figure 2, can be presented on a semi-logarithmic plot where the coordinates of $\log C/C_0$ vs. time give a straight line relationship (see Figure 3). The rate constants for the loss of BHA are determined from their gradient and were calculated by Equation (2). The rate constants for each temperature are tabulated in Table 6.

Figure 4 is the Arrhenius plot of $\log K$ vs. $1/T(^{\circ}K)$ and shows the temperature dependence of the rate constant for the loss of BHA from the HDPE film. The activation energy was calculated by Equation (3). The numerical value (15.15 Kcal/mole) of the activation energy is also tabulated in Table 6.

Table 1. Loss of BHA from HDPE film at 10°C

Initial BHA concentration (Wt/Wt %), Co	Weight of film sample (g)	Time interval (days), t	BHA concentration after time t (Wt/Wt %), C	Relative %* of BHA (C/Co x 100) (%)
0.14	5	1	0.127	90.7
		2	0.111	79.3
		3	0.104	74.3
		5	0.085	60.7
		7	0.071	50.7

*Value represents relative percent of initial concentration of BHA present in film.

Table 2. Loss of BHA from HDPE film at 22°C.

Initial BHA concentration (Wt/Wt %), Co	Weight of film sample (g)	Time interval (days), t	BHA concentration after time t (Wt/Wt %), C	Relative % of BHA (C/Co x 100) (%)
0.14	5	1	0.112	80.0
		2	0.090	64.3
		3	0.074	52.9
		5	0.045	32.1
		7	0.028	20.0

Table 3. Loss of BHA from HDPE film at 30°C.

Initial BHA concentration (Wt/Wt %), Co	Weight of film sample (g)	Time interval (days), t	BHA concentration after time t (Wt/Wt %), C	Relative % of BHA (C/Co x 100) (%)
0.14	5	0.5	0.110	78.6
		1	0.091	65.0
		2	0.052	37.1
		3	0.034	24.3
		5	0.014	10.0
		7	0.005	3.6

Table 4. Loss of BHA from HDPE film at 40°C.

Initial BHA concentration (Wt/Wt %), Co	Weight of film sample (g)	Time interval (days), t	BHA concentration after time t (Wt/Wt %), C	Relative % of BHA (C/Co x 100) (%)
0.14	5	0.25	0.104	74.3
		0.5	0.076	54.3
		1	0.045	32.1
		1.5	0.025	17.9
		2	0.018	12.9
		3	0.005	3.6

Table 5. Loss of BHA from HDPE film at 50°C.

Initial BHA concentration (Wt/Wt %), Co	Weight of film sample (g)	Time interval (days), t	BHA concentration after time t (Wt/Wt %), C	Relative % of BHA (C/Co x 100) (%)
0.14	5	0.25	0.076	54.3
		0.5	0.034	24.3
		0.75	0.014	10.0
		1	0.007	5.0
		1.5	0.005	3.7

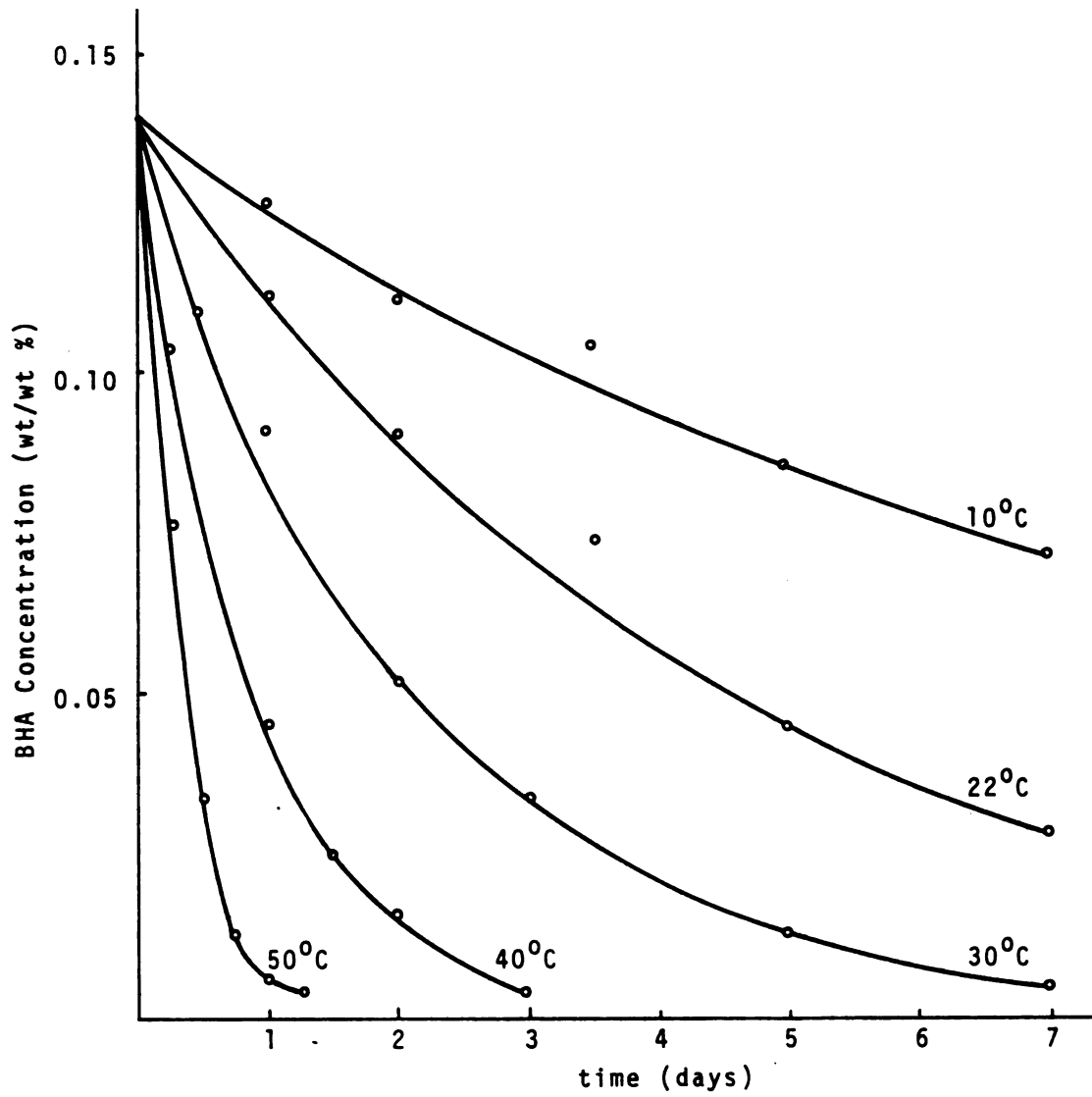


Figure 2. The change in concentration of BHA as a function of storage time for the respective temperature of test.

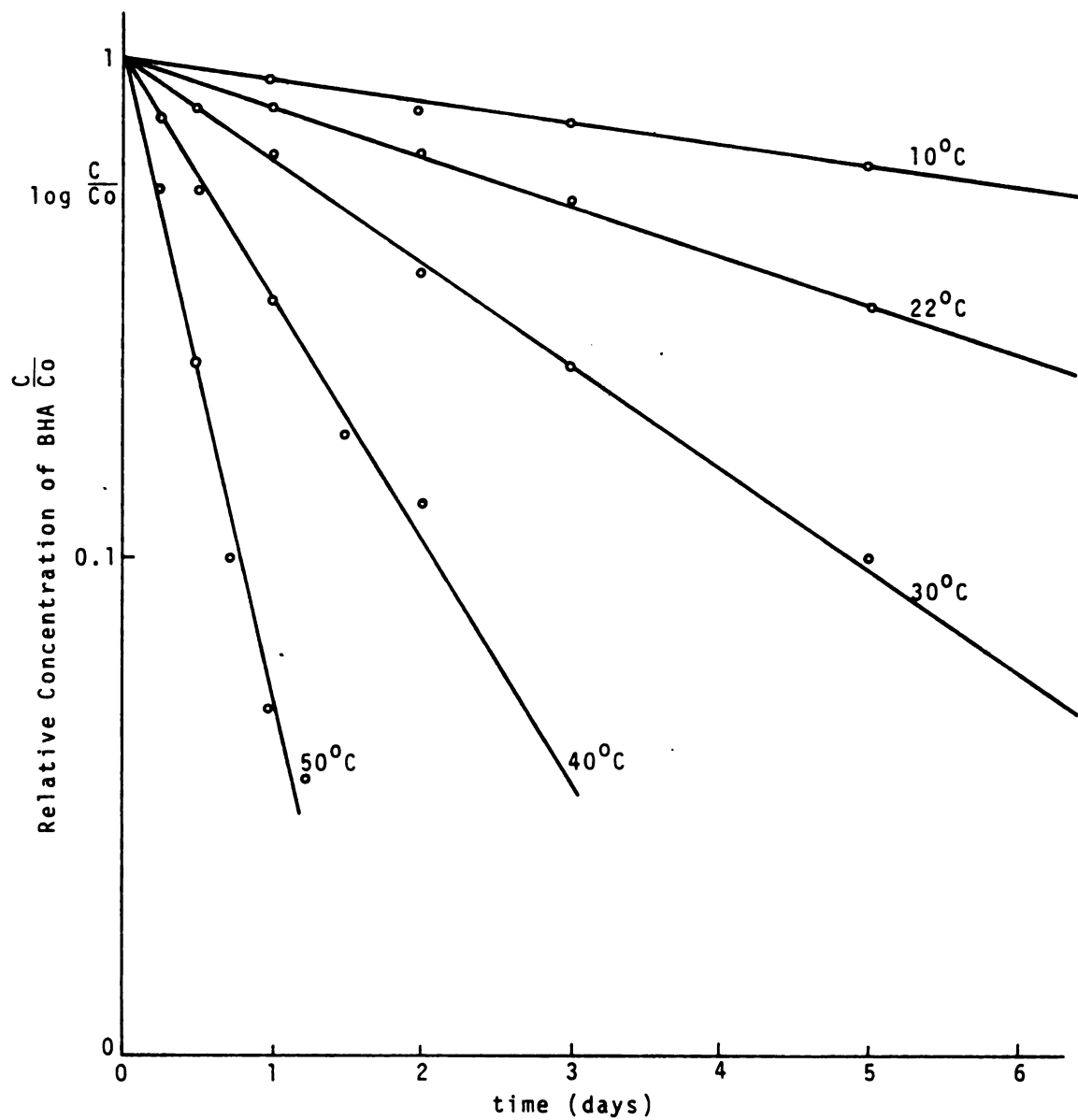


Figure 3. A first order rate plot of the loss of BHA from HDPE film samples as a function of test temperature.

Table 6. The rate constants of loss of BHA from the HDPE film and the activation energy.

Temperature (°C)	Rate constant of loss, $k \times 10^{-3}$	Activation Energy (Kcal/mole)
10	4.04	
22	9.58	
30	19.62	15.15
40	45.67	
50	121.76	

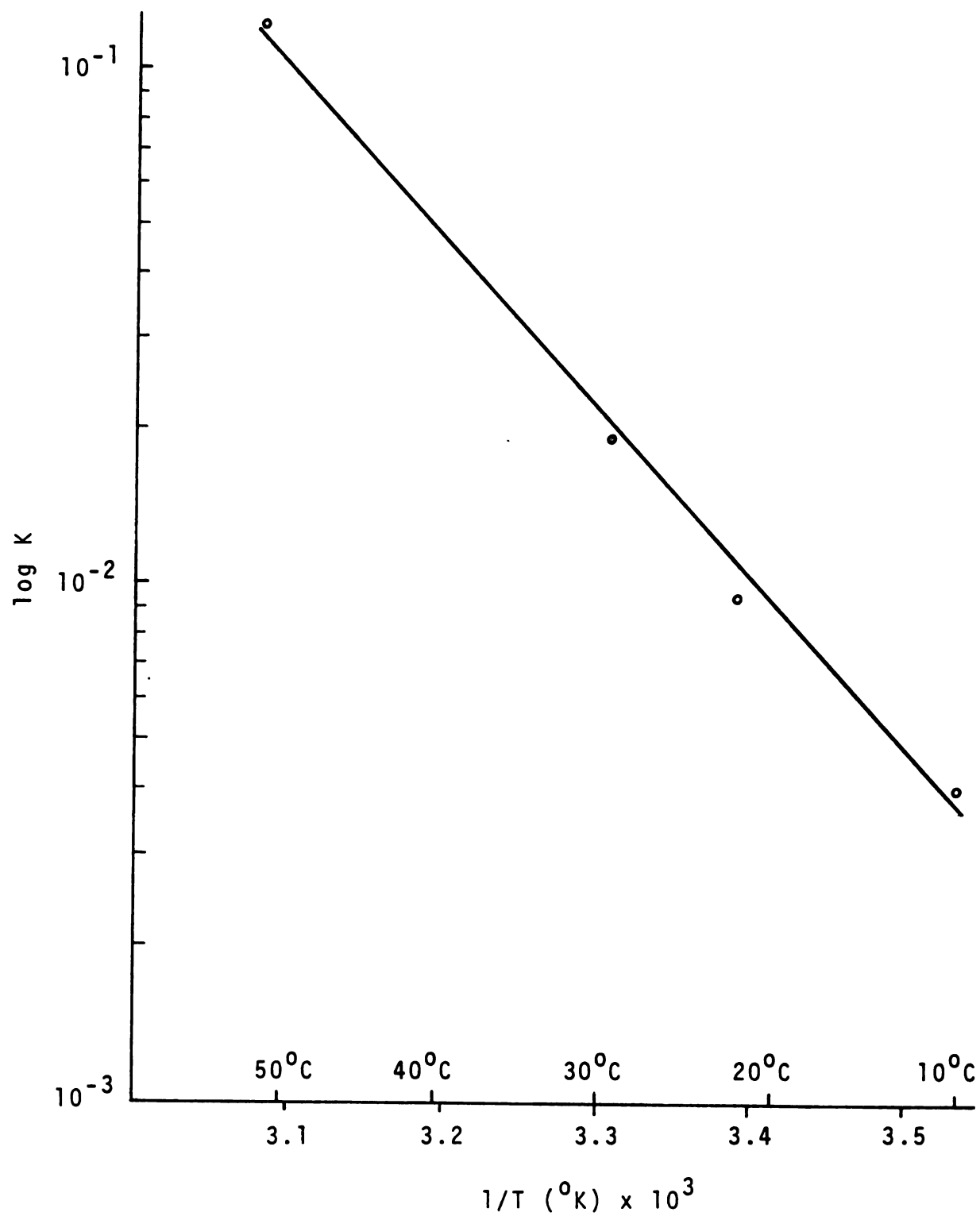


Figure 4. Temperature dependence on the rate constants for the loss of BHA from HDPE film (Arrhenius plot).

Table 7 shows 90% loss ($C/C_0 \times 100 = 90\%$) time of BHA from the film, which was estimated by the rate constants of loss for each temperature and Equation (2). These data will be used to estimate the diffusion coefficient and the mass transfer coefficient of BHA.

Table 7. Estimation of 90% loss time of BHA from the HDPE film.

Temperature (°C)	Rate constants of loss, $k \times 10^{-3}$ (1/hr)	Estimated time of 90%* loss of BHA from the film, t (days)
10	4.04	23.75
22	9.58	10.01
30	19.62	4.89
40	46.56	2.06
50	121.76	0.79

*from the equation $\ln C/Co = -kt$.

DISCUSSION

BHA Degradation Study

In an initial phase of this study, an attempt was made to separate and identify major oxidation products of BHA formed in polyethylene film as a function of processing and storage environmental conditions.

Since the results of the studies dealing with the isolation and identification of BHA degradation products found during thermal processing were not definite, they will be discussed briefly without detailed procedure or data.

Two types of HDPE resin, one a pure HDPE resin and the other containing a high content of BHA (3% wt/wt), were obtained from a commercial source. To study the thermal degradation of BHA in HDPE at high temperature, resins were mixed and extruded with a laboratory type extruder to give HDPE film, which contained about 0.5% (wt/wt) BHA, at a temperature range between 200-300°C.

Sample film was analyzed according to the procedure previously described in the Experimental section. No degradation products were detected.

To study the photochemical induced degradation of BHA in HDPE film, the same commercial HDPE film that was used

in the loss rate study was employed. Film samples were stored under U.V. light for periods of 1-4 weeks.

Sample film was also analyzed by the procedure described in the Experimental section.

For both cases, it was not possible to isolate or identify degradation products. However, it was found that the loss of BHA occurred very rapidly.

Loss of BHA from HDPE Film

Ideally, an antioxidant should be lost from the polymer film only through direct reaction with propagating radicals. However, there are several other factors which may contribute to antioxidant failure. Evaporation of the antioxidant during resin compounding and from the polymer film during normal use may also be responsible for antioxidant failure.

The loss of BHA from the HDPE film, under the storage conditions employed in the study, has been summarized in Tables 1 to 5 and presented graphically in Figure 2. As shown in Tables 3, 4 and 5, nearly all of the BHA was lost within 1 day at 50°C, 3 days at 40°C, and 7 days at 30°C. The results of the studies carried out at ambient temperature (22°C) indicated that the rate of loss of BHA from HDPE film is much faster than that desired, when BHA is used as a stabilizer for the film. The results show the relationship between the rate of BHA loss and temperature

as presented by the Arrhenius plot. The rate constants for the loss of BHA from the HDPE film, assuming other conditions being the same, increased with increased storage temperature.

Modeling of the BHA Loss Process

In developing a mathematical model for expressing the rate of loss of BHA from HDPE film, the boundary conditions were established based on several assumptions. In this case, the model was based directly on a derivation presented by Crank (1975). A slightly modified form of a derivation by Calvert and Billingham (1979) was then applied to estimate the diffusion coefficient (D) of BHA in the HDPE film and the mass transfer coefficient (α) of BHA from the HDPE film surface.

It was assumed that the film sample under test contained a single additive, BHA, which was homogeneously dissolved in the film at a concentration below saturation, and that the additive is lost to the flowing medium in contact with the film surface (excluding chemical reactions). This results in the additive concentration immediately above the film surface to be maintained continuously at zero. In this experiment the flowing medium was air.

The simplest assumption is that the rate of loss is directly proportional to the difference between the actual concentration (C_s) at the surface at any time (t) and the

concentration (C_e) which would be in equilibrium with the surrounding atmosphere. Mathematically this means that the boundary condition at the surface of film is equal to

$$-D \frac{\partial C}{\partial X} = \alpha (C_e - C_s) \quad 4)$$

where α is a constant of proportionality.

For the loss of additives from a polymer, the proportionality constant was described by Angert et al. (1961), who pointed out that the rate of loss of additive was determined by two factors. Initially, the loss rate is determined by the rate of volatilization of the additive from the polymer surface, which will act to create a concentration gradient at the surface. Subsequently, material depleted from the surface must be replaced by diffusion from the bulk so that the overall loss process depends upon both the rate of mass transfer across the sample surface and the rate of diffusion within the film sample. In this study the rate of mass transfer of BHA across the film surface is called the mass transfer coefficient and is the proportionality constant.

It can be said that the additive is lost by surface evaporation at a rate determined by the surface concentration and the parameter α , the lost additive being replaced at the surface by diffusion from the bulk with a diffusion coefficient D . Under these conditions, Crank (1975) has shown that the total amount of additive (M_t) leaving the

polymer up to time (t) is expressible as a fraction of the corresponding amount (M^∞) leaving at infinite time by

$$\frac{M_t}{M^\infty} = 1 - \sum_{n=1}^{\infty} \frac{2L^2 \cdot \exp(-\beta_n^2 \cdot T)}{\beta_n^2 (\beta_n^2 + L^2 + L)} \quad 5)$$

where $T = Dt/\ell^2$

$L = \ell\alpha/D$

ℓ = half of film thickness, cm

t = time, sec.

D = diffusion coefficient of additive in polymer cm^2/sec

α = mass transfer coefficient of additive from polymer, cm/sec

and the β_n values are the positive roots of

$$\beta_n \tan \beta_n = L \quad 6)$$

which are given by Carslaw and Jaeger (1959).

A graph showing $(1-M_t/M^\infty)$ vs. T for several values of L is presented in Figure 5 from the numerical value tabulated by Newman (1931)*. Equation 5 can be solved by using Figure 5 for certain values of L by selecting the T value correctly.

Clearly, the most important parameter for additive loss from the polymer is the quantity L , since this parameter will determine whether additive loss is dominated by diffusion or by evaporation from the surface.

*Appendix 1

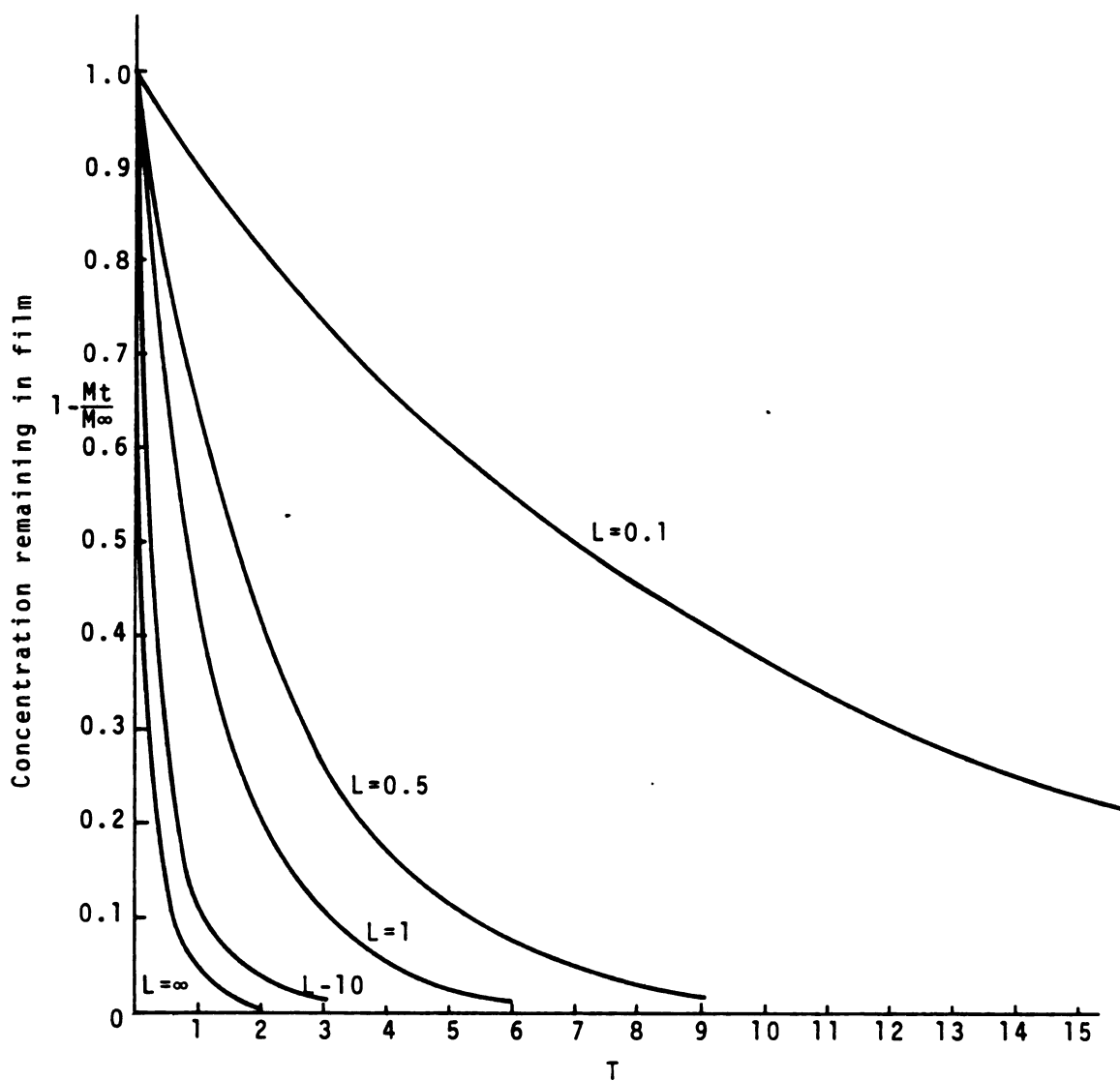


Figure 5. Theoretical concentration of BHA in the film after time t vs. $T (=Dt/l^2)$ for selected L values.

The mass transfer coefficient (α) is given by the expression,

$$V = \alpha \cdot C_s \quad 7)$$

where

V = the rate of volatilization of additive per unit surface area of the polymer, $\text{mg}/\text{cm}^2 \cdot \text{sec}$

C_s = the concentration of additive at the polymer surface, gm/cm^3

By cancellation, it is seen that the dimensions of α are in cm per sec and that the dimensions of α/D would be $1/\text{cm}$. Since ℓ , the half thickness of the film is also expressed in cm, $\ell \cdot \alpha/D$ or L would be a non-dimensional ratio expressed by a single number, the additive loss properties of the film under constant external conditions.

Calvert and Billingham (1979) had pointed out that the loss of a simple low molecular weight additive such as BHT (Butylated Hydroxy Toluene) from thick films and bulk solids is determined by diffusion, while loss from thin films is controlled by the evaporation rate of the additive. In these studies, thin film samples (thickness; 2 mils) and a simple low molecular weight additive, i.e. BHA, were used, so that loss of BHA from HDPE film can be assumed to be controlled by the evaporation rate of additive from the polymer surface.

Calvert and Billingham have also modified equation (5) to predict the 90% loss time of additive from polymer.

For the 90% loss of additive from the polymer, numerical evaluation of Equation (5) quickly reveals that no significant errors are introduced by ignoring terms other than $n=1$. Equation (5) can thus be written to give

$$\frac{2L^2 \cdot \exp(-\beta^2 T)}{\beta^2 (\beta^2 + L^2 + L)} = 0.1 \quad 8)$$

A plot* of Equation (8) shows that at low values of L (thin film, low evaporation rate, high diffusion rate) Equation (8) becomes a line of unit slope obeying the equation $\log L + \log T = 0.383$, from which the 90% loss time of additive is given by

$$t = 2.42 \quad \ell/\alpha \quad (L < 0.6) \quad 9)$$

The diffusion coefficient is unimportant under conditions where L is small. The loss time of the additive from the polymer is determined by the thickness and the rate of evaporation of the additive from the polymer surface.

Previously, 90% loss time of BHA for each temperature was determined and the values tabulated in Table 7. Equation (9) was used to estimate the mass transfer coefficient of BHA from HDPE film. Results are tabulated in Table 8. Further, two $L (= \ell\alpha/D)$ values were chosen to be below $L=0.6$ (0.5 and 0.1) to calculate the diffusion

*Appendix 2

Table 8. The mass transport coefficient and the diffusion coefficients of BHA from and within the HDPE film.

Temperature (°C)	Mass transport coefficient $\alpha \times 10^{-9}$ (cm/sec)	diffusion coefficient $D \times 10^{-11}$ (cm ² /sec)	
		L = 0.5	L = 0.1
10	3.0	1.5	7.6
22	7.1	3.6	18.0
30	14.5	7.4	36.8
40	34.5	17.5	87.6
50	90.1	45.8	228.9

coefficient (D) of BHA within the HDPE film for each temperature. Results are also tabulated in Table 8.

The diffusion model, Equation (5), was calculated by reading the $T (=Dt/l^2)$ values from Figure 5 to correlate with the experimental loss-time data for both $L=0.5$ and 0.1 . The mass transfer coefficient and diffusion coefficient values from Table 8 were used to solve Equation (5). Results* are graphically presented in Figures 7-11 for each temperature.

Calculation by the diffusion model for both $L=0.5$ and 0.1 show reasonably good correlation with the experimental loss-time data. Also these graphs show no significant difference between $L=0.5$ and $L=0.1$, even though the diffusion coefficients for $L=0.1$ are 5 times larger than $L=0.5$.**

It was difficult to select an adequate L value to calculate a diffusion coefficient for BHA within the film, since the two L values were well correlated with the experimental data and the simulated results (Figure 7-11). A reasonable estimation is that the diffusion coefficient of BHA within the HDPE film should be between the values calculated with $L=0.5$ and $L=0.1$ which were tabulated in Table 8.

* Numerical values are presented in Appendix 3.

**Appendix 4.

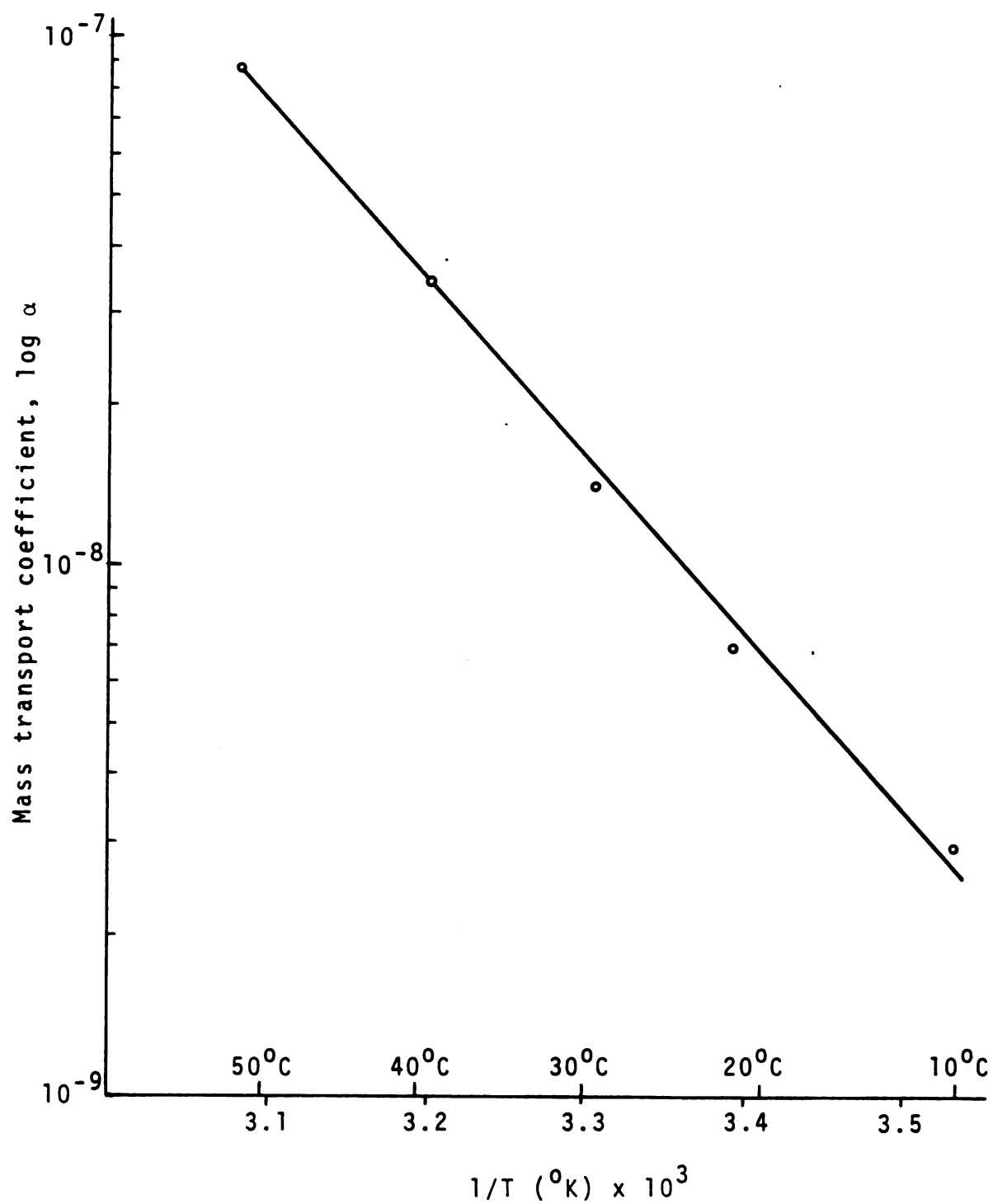


Figure 6. Temperature dependence of the mass transport coefficient of BHA from the HDPE film surface.

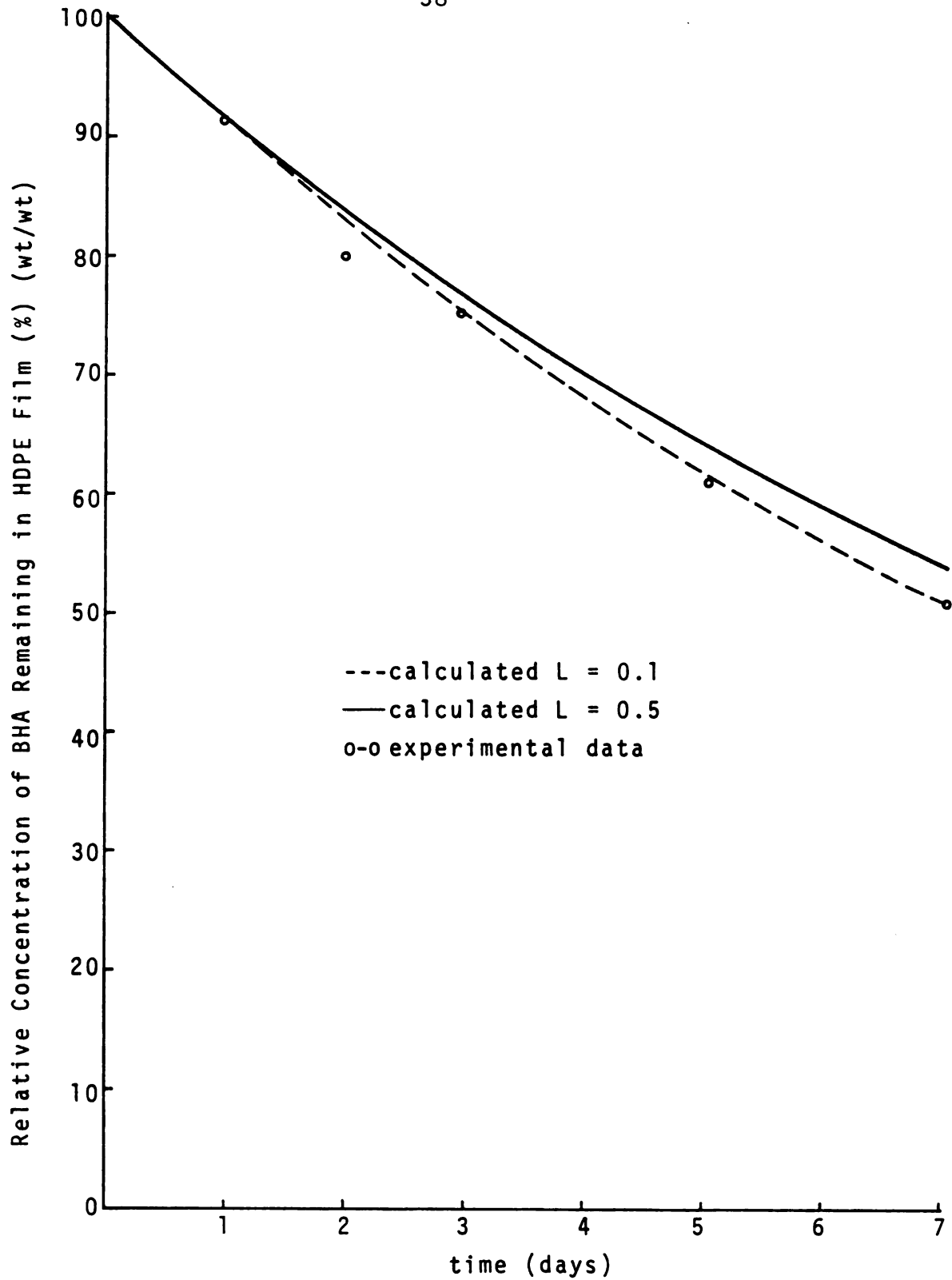


Figure 7. Comparison of simulation and experimental data at 10°C. (BHA concentration change vs. time)

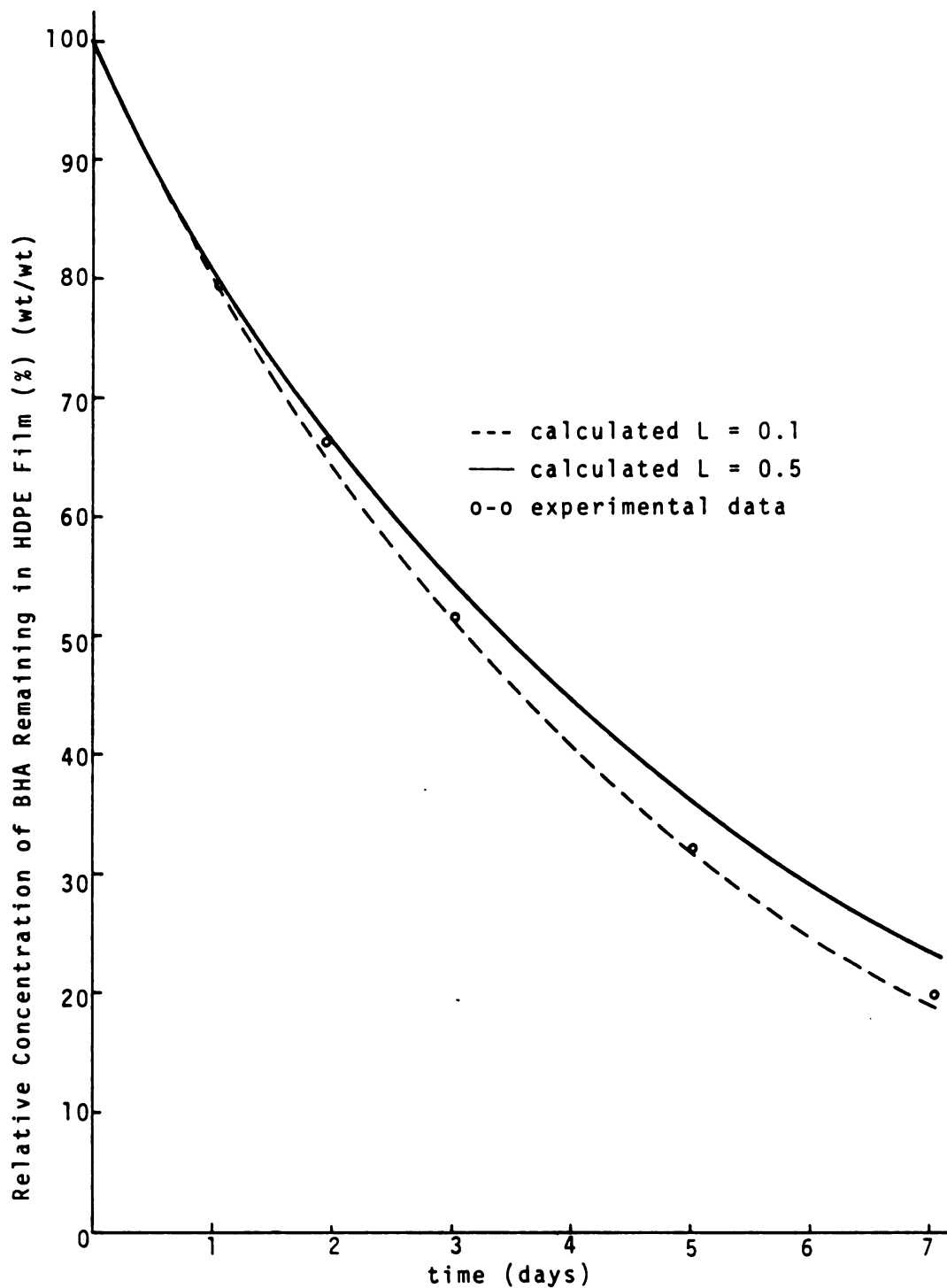


Figure 8. Comparison of simulation and experimental data at 22°C. (BHA concentration change vs. time)

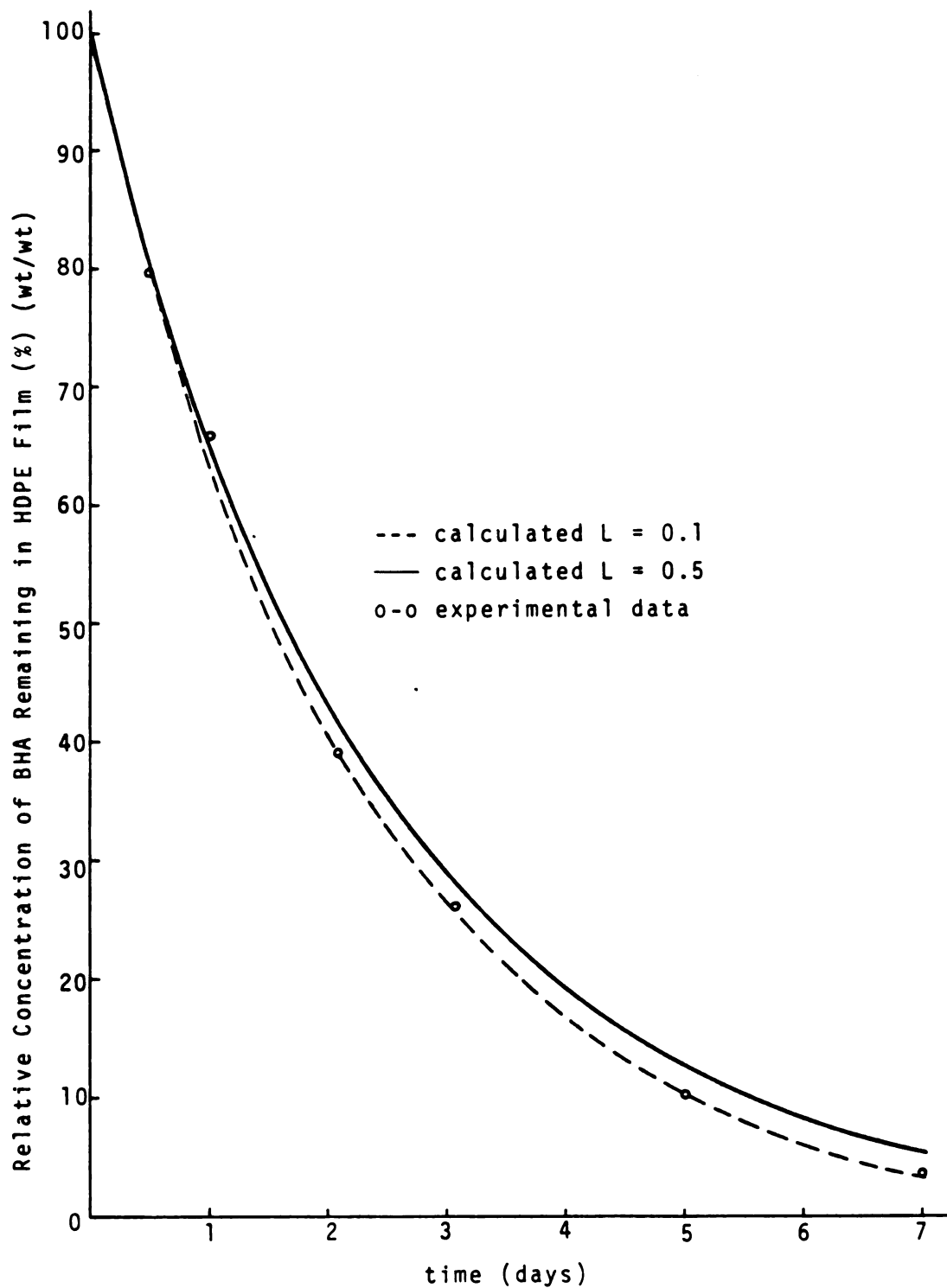


Figure 9. Comparison of simulation and experimental data at 30°C. (BHA concentration change vs. time)

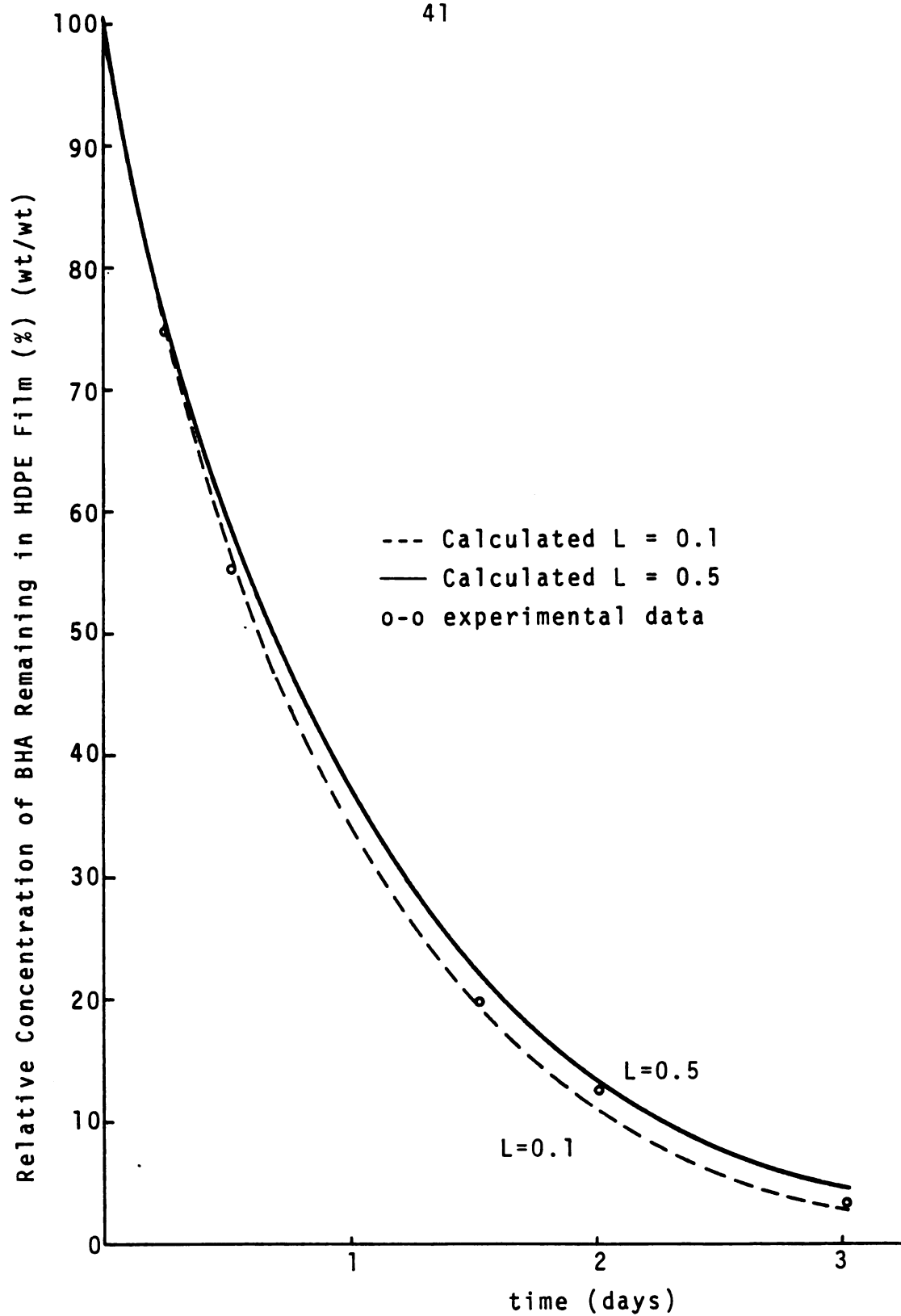


Figure 10. Comparison of simulation and experimental data at 40°C. (BHA concentration change vs. time)

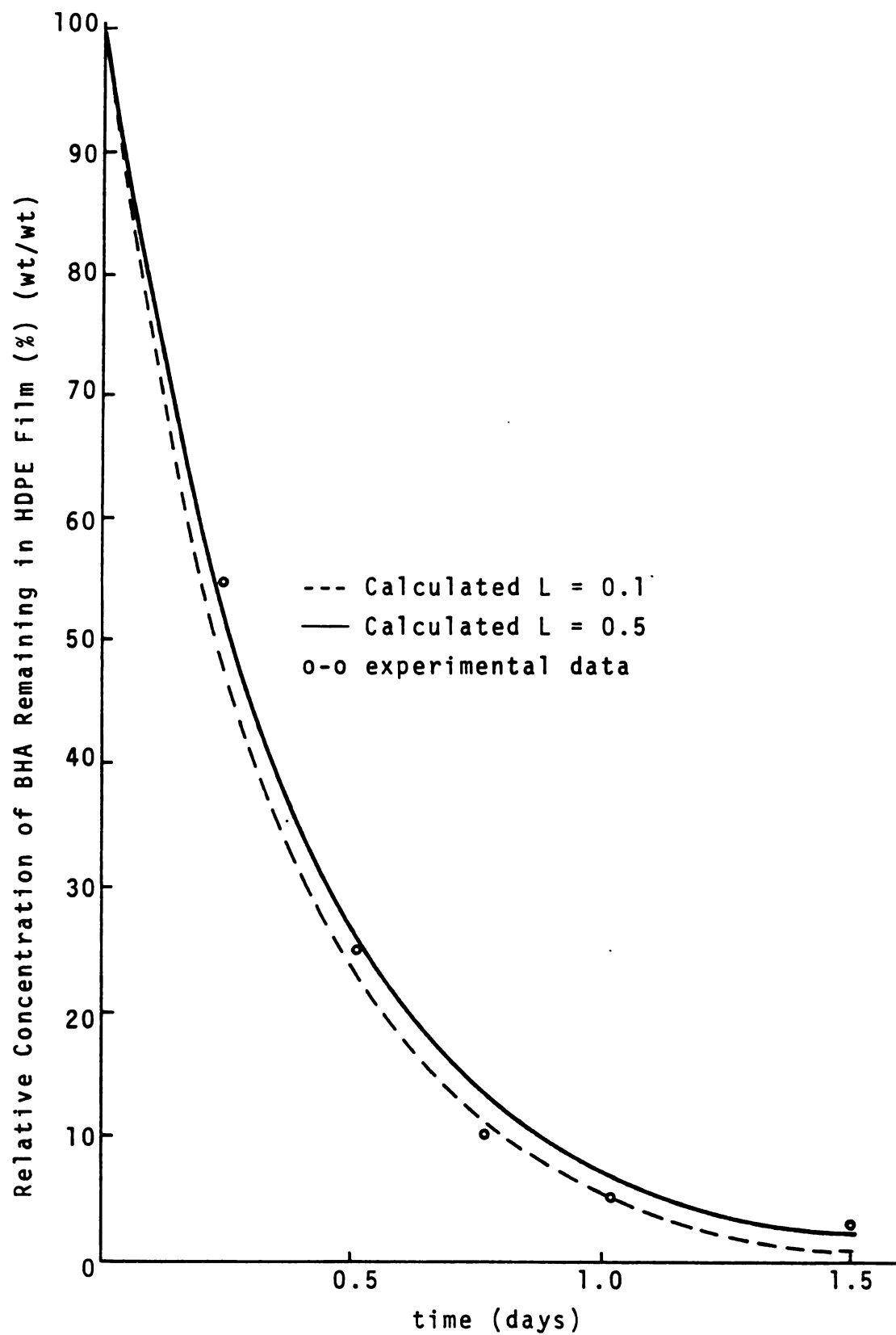


Figure 11. Comparison of simulation and experimental data at 50°C. (BHA concentration change vs. time)

CONCLUSION

The loss of the antioxidant (BHA) from the commercial HDPE film was measured as a function of time and temperature (10-50°C). The BHA loss from the film appeared to follow a first order reaction as a function of time.

By assuming boundary conditions for this experiment it was possible to model the BHA loss process from the HDPE film. The mechanism of additive loss from a polymer was expected to depend upon the diffusion rate of the additive within a polymer and the evaporation rate of the additive from a polymer surface. Both rates were estimated with several assumptions.

An understanding of the transfer mechanism(s) of BHA from packaging film to product would make it possible to better design and select packaging systems for controlled transfer of BHA.

In view of the difficulty of obtaining both the diffusion rate and the mass transfer coefficient of BHA, the estimated values must be regarded as reasonable.

Antioxidant efficiency and good compatibility with a polymer can be ensured by adequate evaluation of antioxidant in terms of its resistance to evaporation by

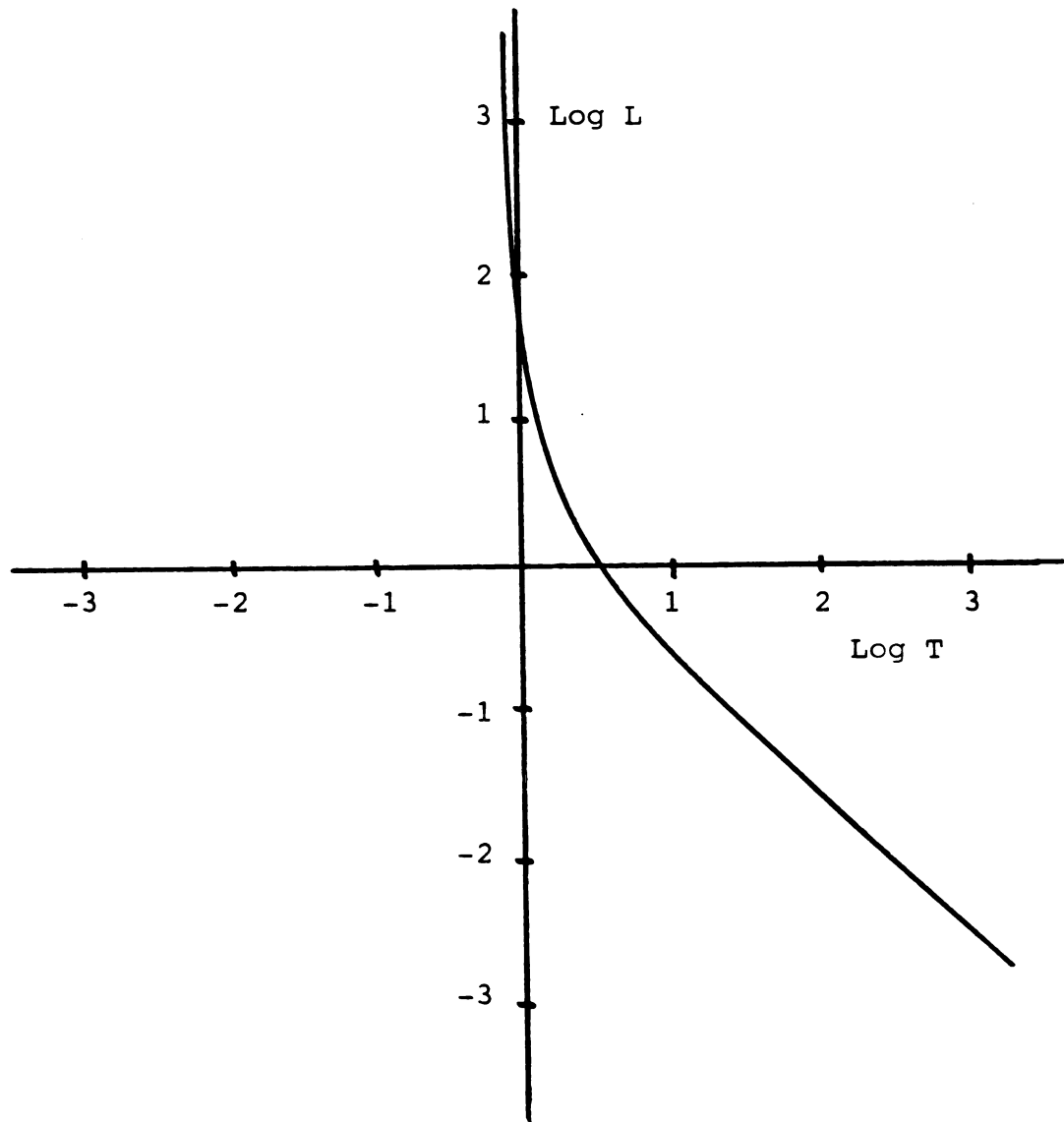
approximating conditions of actual use.

APPENDICES

Appendix 1. Values of $1-Mt/M_{\infty}$ for the slab for selected L values (Newman, 1931).

$T \backslash L$	0.1	0.5	1.0	10.0	∞
.1	0.990	0.952	0.920	0.727	0.643
.2	0.981	0.911	0.851	0.584	0.497
.3	0.971	0.873	0.791	0.483	0.388
.4	0.062	0.836	0.734	0.387	0.298
.5	0.953	0.801	0.682	0.316	0.236
.6	0.944	0.767	0.633	0.258	0.184
.7	0.935	0.735	0.588	0.206	0.144
.8	0.925	0.704	0.546	0.168	0.113
.9	0.917	0.675	0.508	0.136	0.088
1.0	0.908	0.647	0.471	0.114	0.069
1.5	0.865	0.522	0.325	0.041	
2.0	0.824	0.422	0.225	0.0148	0.0058
3.0	0.748	0.274	0.107	0.0019	0.0005
4.0	0.678	0.179	0.051	0.00025	
5.0	0.615	0.120	0.0245		
6.0	0.560	0.0761	0.0117		
7.0	0.508	0.0496	0.0056		
8.0	0.461	0.0323	0.0027		
9.0	0.419	0.0211			
10.0	0.380	0.0141			
15.0	0.234	0.0016			
20.0	0.145	0.0002			
30.0	0.0545				
40.0	0.0209				
50.0	0.0079				

Appendix 2. The plot of Equation (7) expressed in dimensionless coordinates, T and L .



Appendix 3. Predicted concentrations of BHA in HDPE film sample after storage time for $L=0.5$ and $L=0.1$.

Storage temperature (°C)	Storage time, t (days)	L = 0.5			L = 0.1		
		D= /L (cm ² /sec)	T=DT/ ² (%)	C/Co (%)	D (cm ² /sec)	T (%)	C/Co (%)
10±1	1		0.2	91		1.0	91
	2		0.4	83.5		2.0	82
	3	1.5x10 ⁻¹¹	0.6	76.5	7.6x10 ⁻¹¹	3.1	75
	5		1.0	64.5		5.1	62
	7		1.4	54		7.1	51
22±1	1		0.5	81		2.4	80
	2		1.0	65		4.8	62.5
	3	3.6x10 ⁻¹¹	1.5	53	18.0x10 ⁻¹¹	7.2	50
	5		2.4	36		12.1	32
	7		3.4	23		16.9	19
30±1	0.5		0.5	80		2.5	79
	1		1.0	64.5		4.9	62
	2		2.0	42		9.9	38
	3	7.4x10 ⁻¹¹	3.0	27.5	36.8x10 ⁻¹¹	14.8	24
	5		5.0	12		24.6	10.5
40±1	7		7.0	5		34.5	3
	0.25		0.6	76.5		2.9	75.5
	0.5		1.2	59		5.9	56.5
	1	17.5x10 ⁻¹¹	2.4	37	87.6x10 ⁻¹¹	11.7	33
	1.5		3.5	22		17.6	18.5
50±1	2		4.7	13		23.5	11
	3		7.0	5		35.2	3
	0.25		1.5	52		7.7	47.5
	0.5		3.1	26		15.3	22.5
	0.75	45.8x10 ⁻¹¹	4.6	14	228.9x10 ⁻¹¹	23	11.5
	1		6.1	7		30.7	5
	1.5		9.2	2		46	1

Appendix 4. Statistical comparison (t-test) of the simulation data determined for $L=0.5$ and $L=0.1$ with the experimental data.

For each temperature, the differences (absolute values) between the experimental concentrations and concentrations determined by simulation were calculated for both $L=0.5$ and $L=0.1$

Group X includes the differences between the experimental concentrations and simulated concentrations when L is 0.5, while group Y include the values when L is 0.1.

To determine which L value is closer to experimental data, the hypothesis (H_0) was tested that the experimental data indicated that the differences between experimental concentrations and simulated concentrations for $L=0.5$ were larger than the differences between experimental concentrations and simulated concentrations for $L=0.1$.

At 10°C

Experimental concentration	Simulated Concentrations			
	$L=0.5$	differences	$L=0.1$	differences
90.7	91	0.3	91	0.3
79.3	83.5	4.2	82	2.7
74.3	76.5	2.2	75	0.7
60.7	64.5	3.8	62	1.3
50.7	54	3.3	51	0.3
		Group X	Group Y	

X	0.3	4.2	2.2	3.8	3.3
Y	0.3	2.7	0.7	1.3	0.3

$$\bar{X} = 2.76 \quad \bar{Y} = 1.06$$

$$S_p = 1.3155$$

$$T = \frac{\bar{X} - \bar{Y}}{S_p \sqrt{\frac{1}{n_1} + \frac{1}{n_2}}} = 2.043$$

$$H_0 ; \mu_1 = \mu_2$$

$$H_1 ; \mu_1 > \mu_2$$

at $\alpha = 0.05$ and 8 d.f.

$$t = 1.86$$

since $2.043 > 1.86$, H_1 is accepted.

(=group X is larger than group Y)

At 22°C

X	1	0.7	0.1	3.9	3
Y	0	1.8	2.9	0.1	1

Using the same procedure as above

at $\alpha = 0.05$ and 8 d.f.

H_0 is accepted. (Group X is not larger than group Y)

At 30°C

X	1.4	0.5	4.9	3.2	2	1.4
Y	0.4	3	0.9	0.3	0.5	0.6

Using the same procedure

at $\alpha = 0.05$ and 10 d.f.

H_0 is accepted. (Group X is not larger than group Y)

At 40°C

X	2.2	4.7	4.9	4.1	0.1	1.4
Y	1.2	2.2	0.9	0.6	1.9	0.6

Using the same procedure

at $\alpha = 0.05$ and 10 d.f.

H_1 is accepted. (Group X is larger than group Y)

At 50°C

X	2.3	1.7	4	2	1.6
Y	6.8	1.8	1.5	0	2.6

Using the same procedure

at $\alpha = 0.5$ and 8 d.f.

H_0 is accepted. (Group X is not larger than group Y)

Results show that group X (i.e. differences when $L = 0.5$) is larger than group Y at 10°C and 40°C and there is no significant difference at 22°C, 30°C and 50°C.

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