

A Mathematical Model Based on Experimental and Theoretical Aspects of Polyethylene Biodegradation and a Numerical Simulation (ポリエチレン生分解に関する実験と理論に基づく数学モデルと数値シミュレーション)

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1 introduction

Polymeric compounds synthesized from petroleum are regarded in general as chemically inert in the environment. However, recent studies have shown that they can be degraded although the process may generally be slow [1, 2, 3, 4]. In particular, the establishment of applied technologies of biodegradability are expected in various fields including composting and development of environmentally conscious prod-

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ucts. As far as polyethylene (PE) is concerned, PE-utilizing bacteria were obtained by screening of soil bacteria that grew on photo-fragmented PE or PEwax. Nine strains including *Pseudomonas*, *Sphigomonas*, *Stenotrophomonas*, *Acinetobacter* are isolated. Empty PE capsules were made subject to soil burial tests, and PE-utilizing fungi were isolated from those capsules. These fungi were identified as *Aspergillus*, *Penicillium*, *Acremonium* species. These experiments have demonstrated that PE can be biodegraded. However, the precise mechanism of the biodegradation process has not been fully understood. In this paper, we study this problem numerically.

In order to study PE biodegradation experimentally, isolated bacteria and fungi were cultivated using photo-degraded PE or PEwax as the sole carbon source, and the weight distributions of PE before and after cultivation of microorganisms were analyzed with high temperature gel-permeation chromatography (GPC). The experimental results showed that small molecules were consumed faster and that the entire weight distribution was shifted higher. On the other hand, *n*-alkane like PE is known to be metabolized *via* terminal oxidation, diterminal oxidation, or subterminal oxidation. PE molecules carboxylated *via* these metabolic processes become structurally analogous to fatty acid, and become subject to β -oxidation. A PE molecule that undergoes the β -oxidation process loses its components piece by piece as acetic acid (molecular weight of 60) at its terminal in one cycle of β -oxidation.

The foregoing experimental study and theoretical view lead to the following scenario: small PE molecules are directly consumed by microorganism, and large PE molecules lose their components piece by piece *via* β -oxidation until they become small enough to be absorbed directly by cells from a culture medium. A mathematical model based on this scenario was introduced in [5]. We analyzed the model numerically, and here we introduce some numerical results to show how PEwax is biodegraded by *Aspergillus* species.

2 The PE biodegradation model and a linear approximation

We denote the total weight of M -molecules present at time t by $w(t, M)$. Here we call the PE molecules of molecular weight M simply M -molecules. The following PE biodegradation model was proposed in [5].

$$\frac{dx}{dt} = -\rho(M)x - \beta(M)x + \beta(M+L)\frac{M}{M+L}y. \quad (1)$$

Here $x = w(t, M)$, the total weight of M -molecules present at time t , and $y = w(t + L, M)$, the total weight of $(M + L)$ -molecules present at time t . L represents the amount which a PE molecules loses in one cycle of β -oxidation. Since a molecule loses acetic acid (CH_3COOH) at its terminal in one cycle of β -oxidation L is equal to 60. $\rho(M)$ represents the rate of total weight decrease in the class of M -molecules due to direct consumption. $\beta(M)$ represents the rate of the total weight shift from the class of M -molecules to the class of $(M - L)$ -molecules due to β -oxidation. The first term and the second term of the right hand side of (1) can be combined to give the following form.

$$\frac{dx}{dt} = -\alpha(M)x + \beta(M + L) \frac{M}{M + L}y, \quad (2)$$

where

$$\alpha(M) = \rho(M) + \beta(M).$$

Suppose that the initial weight distribution is given by the function $f(M)$. Then the solution $x = w(t, M)$ of (1) must satisfy the initial condition

$$w(0, M) = f(M). \quad (3)$$

(2) and (3) are combined to give the following initial value problem.

$$\begin{cases} \frac{dx}{dt} = -\alpha(M)x + \beta(M + L) \frac{M}{M + L}y, \\ w(0, M) = f(M). \end{cases} \quad (4)$$

Under the assumption that $\alpha(M)$ and $\beta(M)$ are monotone non-increasing continuous functions such that

$$0 \leq \beta(M) \leq \alpha(M),$$

and that $f(M)$ is a continuous function such that

$$f(M) = 0 \quad \text{for } M \geq b$$

for some positive constant b , (4) has a unique solution $x = w(t, M)$ [6]. This solution is a continuous function defined on the set

$$\{(t, M) | t \geq 0, M \geq a\},$$

where a is a fixed constant less than b , and satisfies

$$w(t, M) = 0 \quad \text{for } M \geq b.$$

A linear problem whose solution serves as an approximate solution of (4) was obtained in [5]. Consider the $N + 1$ equally spaced points N_i ($i = 0, 1, 2, \dots, N$) given by

$$N_i = a + i\Delta M \quad \left(\Delta M = \frac{b-a}{N} \right).$$

There are a non-negative integer n and a constant R that satisfy

$$L = n\Delta M + R \quad (0 \leq R \leq \Delta M).$$

Then assuming that the solution $w(t, M)$ of (4) is linear with respect to M , the following linear problem is obtained from (4).

$$\begin{cases} \frac{dw_i}{dt} = -\alpha_i w_i + \beta_i w_{i+n} + \gamma_i w_{i+n+1} & (i = 0, 1, 2, \dots, N), \\ w_i(0) = f_i, \end{cases} \quad (5)$$

where

$$\alpha_i = \alpha(M_i),$$

$$\beta_i = \frac{\sigma_i M_i}{M_i + L} \left(1 - \frac{R}{\Delta M} \right),$$

$$\gamma_i = \frac{\sigma_i M_i}{M_i + L} \frac{R}{\Delta M},$$

$$\sigma_i = \left(1 - \frac{R}{\Delta M} \right) \beta(M_{i+n}) + \frac{R}{\Delta M} \beta(M_{i+n+1}),$$

$$f_i = f(M_i).$$

Here $w_i = w(t, M_i)$. The solution $x = w(t, M)$ of the original initial value problem (4) satisfy the linear problem (5) only when $w(t, M)$ is linear with respect to M . However the solution $w_i = w_i(t)$ ($i = 0, 1, 2, \dots, N$) should serve as an approximate solution of the original problem in general even when $w(t, M)$ is nonlinear with respect to M . We define an approximate solution $\tilde{w}(t, M)$ by

$$\tilde{w}(t, M) = \frac{M_{i+1} - M}{\Delta M} w_i(t) + \frac{M - M_i}{\Delta M} w_{i+1}(t) \quad \text{for } M_i \leq M \leq M_{i+1}.$$

The validity of the approximate solution has been established. Let T a fixed positive constant. Then given $\epsilon > 0$, there is a $\delta > 0$ such that

$$\Delta M < \delta \implies |w(t, M) - \tilde{w}(t, M)| \leq \epsilon \quad \forall (t, M) \in [0, T] \times [a, b]$$

3 A computational method for PE biodegradation model

Here we introduce a computational method [6] to analyze the PE biodegradation model. Suppose that the degradation rate $\alpha(M)$ is given. Then there is a $\tilde{M}$ such that $\beta(M)$ is constant for $M \leq \tilde{M}$. Moreover we may assume that $\alpha(M) = \beta(M)$, i.e. $\rho(M) = 0$, for $M \geq \tilde{M}$. Suppose that M_j is a point that is close to $\tilde{M}$. Given some approximate values of $\alpha_i = \alpha(M_i)$ ($i = 0, 1, 2, \dots, N$), we set the following values for $\beta(M_i)$ ($i = 0, 1, 2, \dots, N$) according to the assumption.

$$\beta(M_i) = \begin{cases} \alpha_j & i \leq j, \\ \alpha_i & i > j. \end{cases}$$

Then the coefficients of the linear system of (5) can be evaluated. Let $g(M)$ be the function which represents the PE weight distribution after cultivation. We may assume that the final stage is reached at $t = 1$ so that $g(M) = w(1, M)$. Let

$$g_i = g(M_i) \quad (i = 0, 1, 2, \dots, N).$$

On the other hand the variation-of-constants formula leads to the following condition to be met.

$$g_i = e^{-\alpha_i} f_i + \int_0^1 e^{-\alpha_i(1-s)} [\beta_i w_{i+n}(s) + \gamma_i w_{i+n+1}(s)] ds \quad (i = 0, 1, 2, \dots, N).$$

Once we evaluate the integral numerically, the approximate values of $\alpha_i = \alpha(M_i)$ ($i = 0, 1, 2, \dots, N$) can be redefined by

$$\alpha_i = \log \left(\frac{1}{g_i} \left\{ f_i + \int_0^1 e^{-\alpha_i(1-s)} [\beta_i w_{i+n}(s) + \gamma_i w_{i+n+1}(s)] ds \right\} \right) \quad (i = 0, 1, 2, \dots, N).$$

The numerical computation of α_i ($i = 0, 1, 2, \dots, N$) can be iterated to improve the accuracy of the approximation.

We applied the method described above to the GPC profiles of PEwax obtained before and after 5-week cultivation of *Aspergillus* species. Figures 1 and 2 show some numerical results. Figure 1 shows numerically generated graphs of $\alpha(M)$ and $\beta(M)$. Figure 2 shows the temporal change of the PEwax weight distribution. In the numerical analysis to obtain these results, we set $\tilde{M} = 1500$ and $N = 10000$. We also assumed that the degradation rate $\alpha(M)$ is represented by the exponential function:

$$\alpha(M) = e^{c_1 M + c_2}$$

for all small M , and evaluated the constants c_1 and c_2 numerically applying a least square approximation at each step of iterative computations.

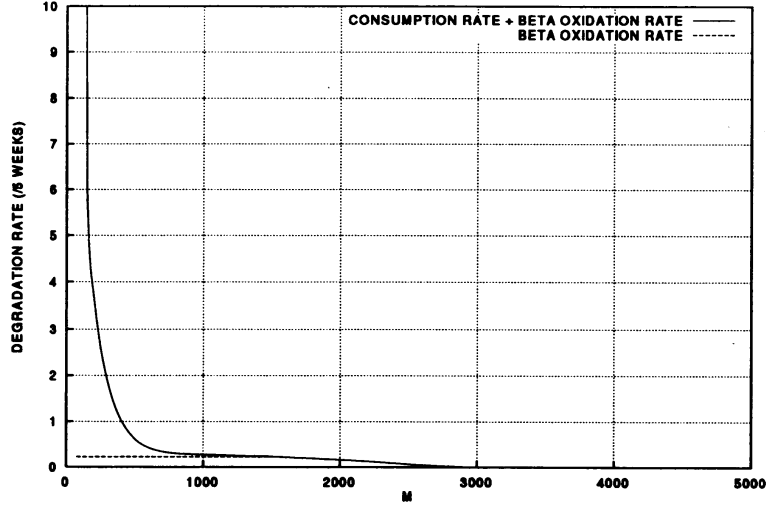


Fig 1: The total degradation rate $\alpha(M)$ and the β -oxidation rate $\beta(M)$ of *Aspergillus* sp. cultivated on PEwax.

4 Discussion

In construction of our mathematical model for PE biodegradation, we assumed that an initial oxidation yielded carboxylated acid for hydrocarbon to become subject to β -oxidation. We also assumed that small PE molecules were consumed faster than the large ones. Thus our mathematical model is based on two primary factors: the direct consumption of small molecules and the weight loss of large molecules due to β -oxidation. One may speculate on Figure 1 that PE molecules of molecular weight over 1000 gradually lose their components undergoing the β -oxidation until they become small enough to be consumed directly by microorganisms. One may also speculate that the direct consumption is more effective for smaller molecules. Note that the match between the numerical result and the experimental result of Figure 2 seems almost perfect, and the result of the numerical simulation well supports the assumption on which our mathematical model is based.

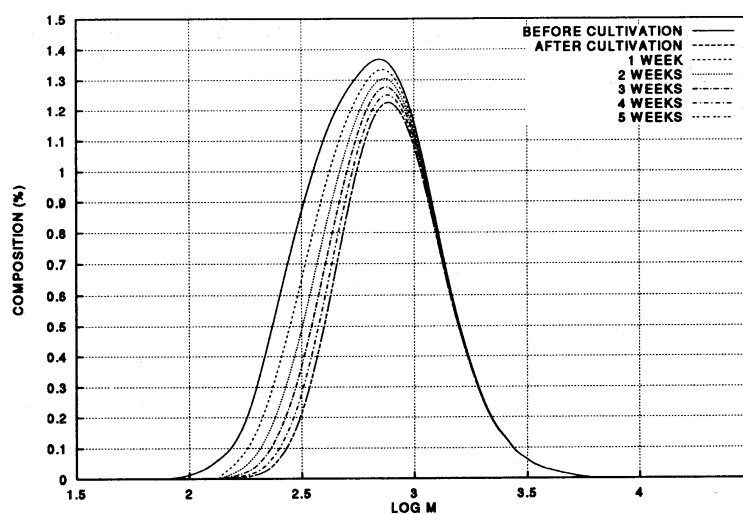


图 2: The temporal change of PEwax weight distribution in 5-week cultivation of *Aspergillus* sp.

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