

# Numerical study of biodegradation of xenobiotic polymers based on exogenous depolymerization model with time dependent degradation rate

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A mathematical model for exogenous depolymerization with time dependent degradation rate is analyzed in order to study the biodegradation of polyethylene glycol. The weight distribution with respect to the molecular weight before and after cultivation of microorganisms were analyzed an inverse problem to determine the time dependent degradation rate. Numerical techniques to solve the inverse problem and to simulate the transition of the weight distribution are described.

**Key words:** *biodegradation, polyethylene glycol, mathematical model, numerical simulation*

## 1 INTRODUCTION

Microbial depolymerization processes are generally classified into either one of two types: exogenous type or endogenous type. In an exogenous depolymerization process, monomer units are separated from the terminals of molecules stepwise. The  $\beta$ -oxidation of polyethylene (PE) is an example of exogenous depolymerization process. Microbial depolymerization processes of PE are based on two primary factors: the gradual weight loss of large molecules due to the  $\beta$ -oxidation and the direct consumption or absorption of small molecules by cells. On the other hand, one of characteristics of endogenous depolymerization processes is the rapid breakdown of large molecules due to internal separations to yield small molecules. The enzymatic degradation of polyvinyl alcohol (PVA) is an example of endogenous depolymerization process. Mathematical models for those depolymerization processes have been proposed, and those models are analyzed to study the biodegradation of the xenobiotic polymers.

In this paper, the analytical and numerical study of exogenous depolymerization processes is continued to analyze the biodegradation of PEG. PEG is one of polyethers which are represented by the expression  $\text{HO}(\text{R-O})_n\text{H}$ , *e.g.*, PEG:  $\text{R} = \text{CH}_2\text{CH}_2$ , polypropylene glycol (PPG):  $\text{R} = \text{CH}_3\text{CHCH}_2$ , polytetramethylene glycol (PTMG):  $\text{R} = (\text{CH}_2)_4$  [5]. Those poly-

mers are utilized for constituents in a number of products including lubricants, antifreeze agents, inks, and cosmetics. They are either water soluble or oily liquid, and eventually discharged into the environment through sewage, and therefore it is especially important to evaluate their biodegradability appropriately.

PEG is produced more than any other polyether, and its major part is consumed in production of non-ionic surfactants. PEG is depolymerized by releasing  $\text{C}_2$  compounds, either aerobically or anaerobically [6, 7, 15]. Figure 1 shows the weight distribution of PEG before and after cultivation of microbial consortium E1 for one day, three days, five days, seven days, and nine days.

In the previous studies [14, 17, 18, 21] on biodegradation of PEG, the degradation rate was assumed to be independent of time. The time dependent degradation rate was considered in a recent study [19]. The time dependent degradation rate was considered in a recent study of endogenous depolymerization [20, 21]. In this paper, the mathematical study of biodegradation of PEG is continued with the time dependent degradation rate incorporated into the exogenous depolymerization model. A change of variable reduces the model into the one for which the degradation rate is time independent. The techniques developed previously were applied to solve an inverse problem of an initial value problem to determine the time independent degradation rate for which the solution of the initial value problem satisfies not only the initial weight distribution but also the weight distribution after cultivation. The time factor was found by assuming the

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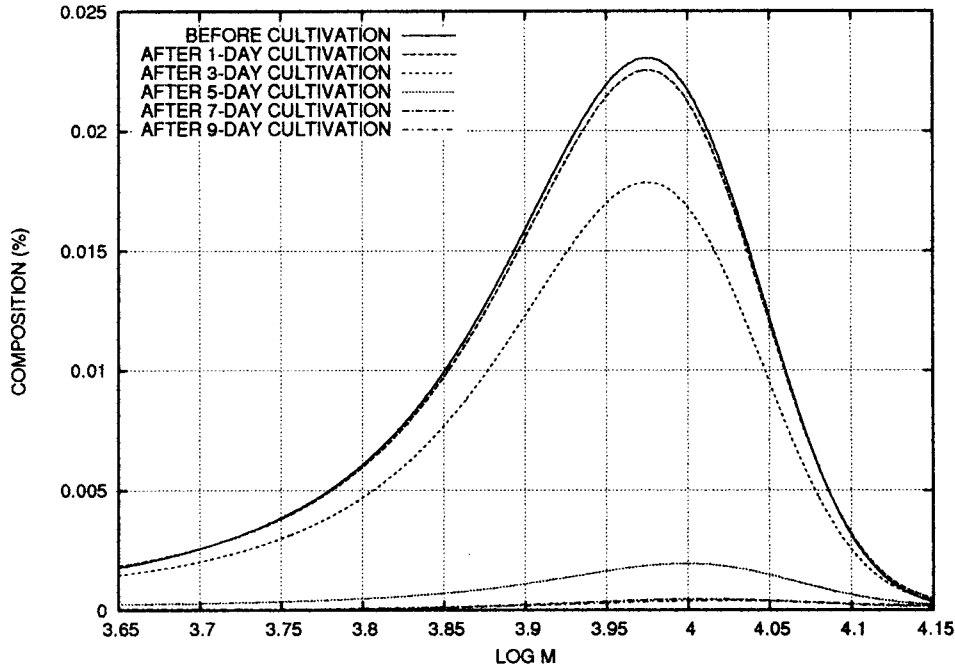


Figure 1: weight distribution of PEG before and after cultivation of microbial consortium E1.

exponential growth of the microbial population. Once the degradation rate was found, the transition of the weight distribution was simulated by solving the initial value problem numerically.

## 2 MODEL FOR PEG BIODEGRADATION

The PE biodegradation model (1) is based on two essential factors: the gradual weight loss of large molecules due to the terminal separation ( $\beta$ -oxidation) and the direct consumption by small molecules by cells [3, 4, 11].

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

Here  $t$  and  $M$  represent the time and the molecular weight respectively. Let a  $M$ -molecule be a molecule with molecular weight  $M$ . Then  $x = w(t, M)$  represents the total weight of  $M$ -molecules present at time  $t$ . The parameter  $L$  represents the amount of the weight loss due to the  $\beta$ -oxidation. The variable  $y$  is given by  $y = w(t, M+L)$  so that it is the total weight of  $(M+L)$ -molecules present at time  $t$ . The function  $\alpha(M)$  is given by  $\alpha(M) = \rho(M) + \beta(M)$ . The function  $\rho(M)$  represents the direct consumption rate, and the function  $\beta(M)$  represents the rate of the weight conversion from the class of  $M$ -molecules to the class of  $(M-L)$ -molecules due to the  $\beta$ -oxidation. The left-hand side of the equation (1) represents the rate of change in the total weight of  $M$ -molecules. The first term on the right-hand side of the equation (1) represents the amount lost by the direct consumption and the  $\beta$ -oxidation in the total weight of  $M$ -molecules per

unit time, and the second term represents the amount gained by the  $\beta$ -oxidation of  $(M+L)$ -molecules per unit time.

The mathematical model (1) was originally developed for the PE biodegradation, but it can also be viewed as a general biodegradation model involving exogenous depolymerization processes. In the exogenous depolymerization of PEG, a PEG molecule is first oxidized at its terminal, and then an ether bond is split. It follows that  $L = 44$  ( $\text{CH}_2\text{CH}_2\text{O}$ ) in the exogenous depolymerization of PEG. It is appropriate for the depolymerization processes over the period after the microbial population reaches the steady state. It has been suggested that the microbial population should be taken into consideration for the period before the microbial population reaches the steady state. Then the degradation rate should be proportional to the microbial population, and the exogenous depolymerization model should take the form:

$$\frac{dx}{dt} = -\sigma(t)\lambda(M)x + \sigma(t)\lambda(M+L)\frac{M}{M+L}y. \quad (2)$$

The solution  $x = w(t, M)$  of (2) is associated with the initial condition:

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

where  $f(M)$  is some prescribed function that represents the initial weight distribution. Given the degradation rate  $\beta(t, M)$ , the equation (2) and the initial condition (3) form an initial value problem to find the unknown function  $w(t, M)$ . On the other hand, given the initial condition (3) and an additional condition

$$w(T, M) = g(M), \quad (4)$$

for some  $T > 0$ , an inverse problem is formulated to determine the degradation rate  $\beta(t, M)$  for which the solution  $w(t, M)$  of the initial value problem (2) and (3) also satisfies the final condition (4).

Let

$$\tau = \int_0^t \sigma(s) ds,$$

and

$$W(\tau, M) = w(t, M),$$

$$X = W(\tau, M),$$

$$Y = W(\tau, M + L).$$

Then

$$\begin{aligned} \frac{dX}{d\tau} &= \frac{dx}{dt} \frac{dt}{d\tau} \\ &= \frac{1}{\sigma(t)} \left\{ -\sigma(t) \lambda(M) x + \sigma(t) \lambda(M + L) \frac{M}{M + L} y \right\} \\ &= -\lambda(M) x + \lambda(M + L) \frac{M}{M + L} y \\ &= -\lambda(M) X + \lambda(M + L) \frac{M}{M + L} Y. \end{aligned}$$

The initial value problem is to find the solution of the equation

$$\frac{dX}{d\tau} = -\lambda(M) X + \lambda(M + L) \frac{M}{M + L} Y \quad (5)$$

subject to the initial condition

$$W(0, M) = f(M). \quad (6)$$

The inverse problem is to find the degradation rate  $\lambda(M)$  for which the solution of the initial value problem (5), (6) also satisfies the final condition

$$W(\mathcal{T}, M) = g(M), \quad (7)$$

where

$$\mathcal{T} = \int_0^T \sigma(s) ds \quad (8)$$

The inverse problem consisting of the equations (5), (6), and (8) was solved numerically. Figure 2 shows the graph of the function  $\lambda(M)$  based on the weight distribution before and after cultivation for three days [18]. Figure 3 shows numerical results for the initial value problem (5) to simulate the transition of the weight distribution for 50 days.

### 3 SIMULATION FOR PEG BIODEGRADATION

Let

$$\tau = S(t) \approx \int_0^t \sigma(s) ds \quad (9)$$

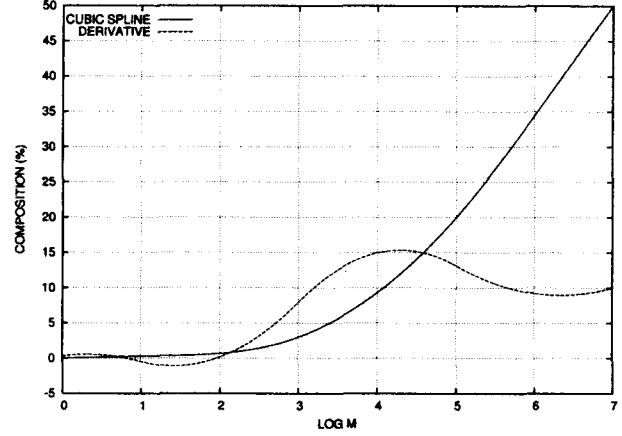


Figure 4: Cubic spline and its derivative based on the data (10).

be the cubic spline determined by  $n$  data points  $(t_1, \tau_1)$ ,  $(t_2, \tau_2)$ ,  $\dots$ ,  $(t_n, \tau_n)$  with the conditions

$$S'(t_1) = \frac{\tau_2 - \tau_1}{t_2 - t_1}, \quad S'(t_n) = \frac{\tau_n - \tau_{n-1}}{t_n - t_{n-1}}.$$

Figure 4 shows the graph of  $S(t)$  and  $S'(t)$  with  $n = 5$ , and

$$\begin{aligned} t_1 = 0, \quad t_2 = 1, \quad t_3 = 3, \quad t_4 = 5, \quad t_5 = 7, \\ \tau_1 = 0, \quad \tau_2 = 0.3, \quad \tau_3 = 3, \quad \tau_4 = 30, \quad \tau_5 = 50. \end{aligned} \quad (10)$$

Once the degradation rate  $\sigma(t) \lambda(M)$  is given, the initial value problem (2) and (3) can be solved directly to see how the numerical results and the experimental results agree. Here the initial value problem was solved numerically with techniques base on previous results [4, 11, 12].

Choose a positive integer  $N$  and set

$$M_i = a + i\Delta M, \quad i = 0, 1, 2, \dots, N \quad \left( \Delta M = \frac{b-a}{N} \right).$$

An approximate solution of the differential equation (1) at  $M = M_i$  is denoted by

$$w_i = w_i(t) \quad (i = 0, 1, 2, \dots, N).$$

There is a non-negative integer  $K$  and a constant  $R$  such that  $L = K\Delta M + R$ ,  $0 \leq R < \Delta M$ , and that the inequalities

$$M_{i+K} \leq M_i + L < M_{i+K+1}$$

hold. Then approximate values of  $w(t, M_i + L)$  and  $\beta(M_i + L)$  can be obtained using

$$\begin{aligned} w(t, M_i + L) &\approx \left( 1 - \frac{R}{\Delta M} \right) w(t, M_{i+K}) \\ &\quad + \frac{R}{\Delta M} w(t, M_{i+K+1}), \end{aligned}$$

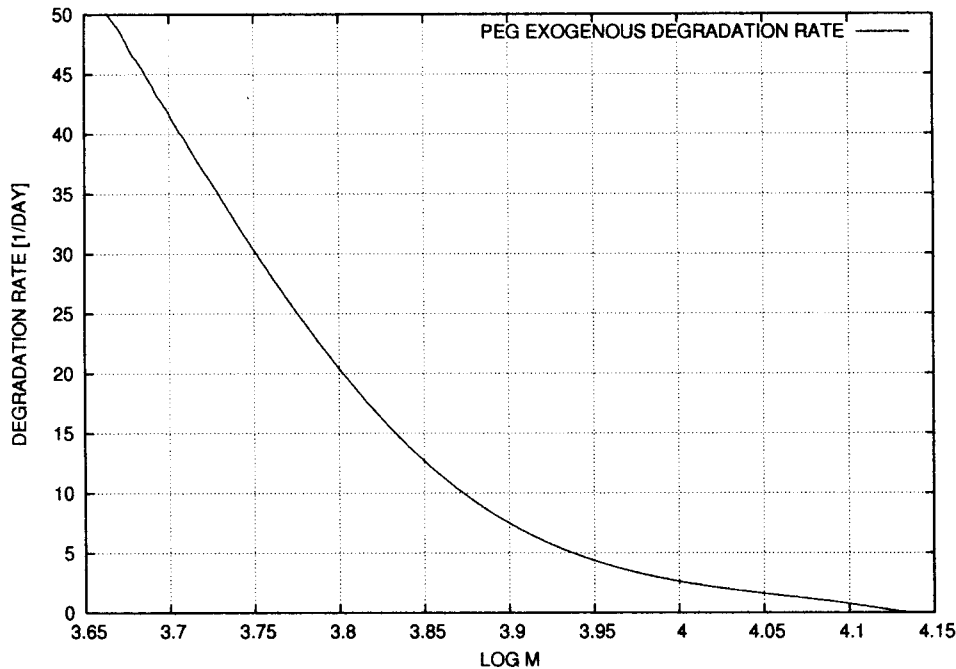


Figure 2: Degradation rate based on the weight distribution of PEG before and after cultivation of a microbial consortium E1 for three days.

$$\lambda(M_i + L) \approx \left(1 - \frac{R}{\Delta M}\right) \lambda(M_{i+K}) + \frac{R}{\Delta M} \lambda(M_{i+K+1}).$$

Substituting these expressions in the differential equation (2) and setting  $M = M_i$ , we obtain the linear system:

$$\frac{dw_i}{dt} = \sigma(t) (-\alpha_i w_i + \beta_i w_{i+K} + \gamma_i w_{i+K+1}), \quad i = 0, 1, 2, \dots, N. \tag{11}$$

Here the coefficients  $\alpha_i$ ,  $\beta_i$ , and  $\gamma_i$  are defined by

$$\begin{aligned} \alpha_i &= \lambda(M_i), \\ \beta_i &= \phi_i \frac{M_i}{M_i + L} \left(1 - \frac{R}{\Delta M}\right), \\ \gamma_i &= \phi_i \frac{M_i}{M_i + L} \cdot \frac{R}{\Delta M}, \\ \phi_i &= \left(1 - \frac{R}{\Delta M}\right) \lambda(M_{i+K}) + \frac{R}{\Delta M} \lambda(M_{i+K+1}). \end{aligned}$$

Approximate values of the degradation rates  $\lambda(M_i)$  can be obtained from the numerical solution of the inverse problem by the linear approximation.

For all sufficiently large  $M$ , the oxidation rate becomes 0. In particular, we may assume that the last two terms on the right-hand side of the equation (11) are absent when  $i + K$  exceeds  $N$ , so that the system (11) becomes a closed system to be solved for unknown

functions  $w_i = w_i(t)$ ,  $i = 0, 1, 2, \dots, N$ . In view of the condition (3), these functions are subject to the initial condition

$$w_i(0) = f_i = f(M_i). \tag{12}$$

Given the initial weight distribution shown in Figure 1, the degradation rate  $\lambda(M)$  shown in Figure 2, and the function  $\sigma(t)$  given by the expression (9) based on the data (10), the initial value problem (11) and (12) was solved numerically implementing the forth-order Adams-Bashforth-Moulton predictor-corrector in PECE mode in conjunction with the Runge-Kutta method to generate approximate solutions in the first three steps [8] by using  $N = 10000$ , and a time interval  $\Delta t = 1/4000$ . Figure (5) shows the numerical result.

### 5 DISCUSSION

In a depolymerization process where the microbial population change, it is necessary to consider the dependence of the degradation rate on time. In this paper, biodegradation of exogenous type was studied by analyzing the exogenous depolymerization model with the time dependent degradation rate. Numerical techniques have been described to solve the inverse problem to obtain the time dependent degradation rate with experimental data introduced into analysis. The time-dependent factor was expressed in terms of cubic spline. The results of numerical simulation has shown that the mathematical techniques to analyze the biodegradation of exogenous type is practically appropriate.

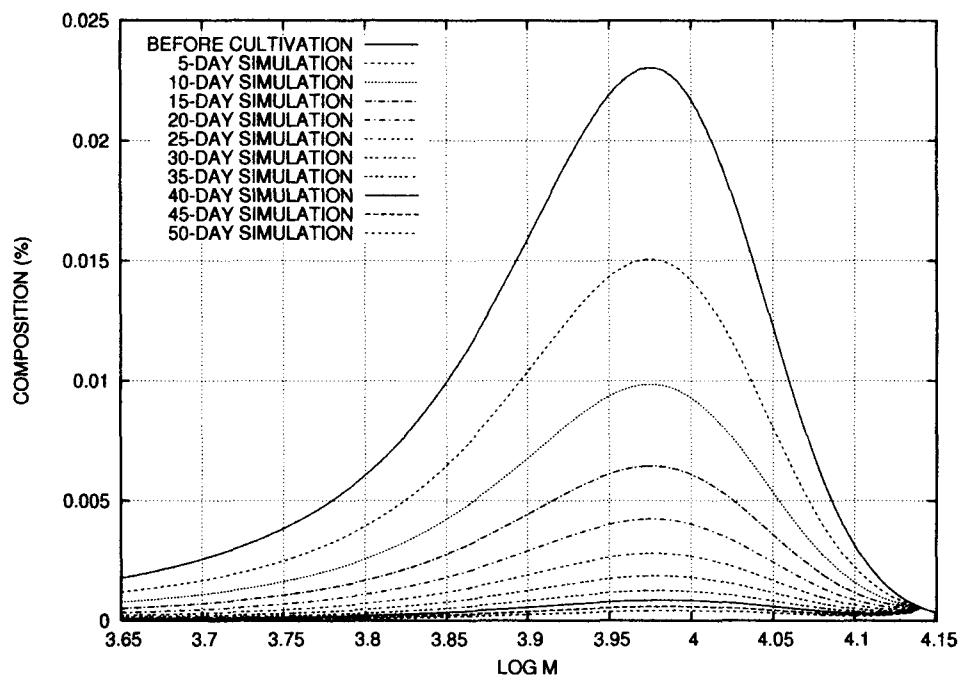


Figure 3: Transition of weight distribution for 50 days.

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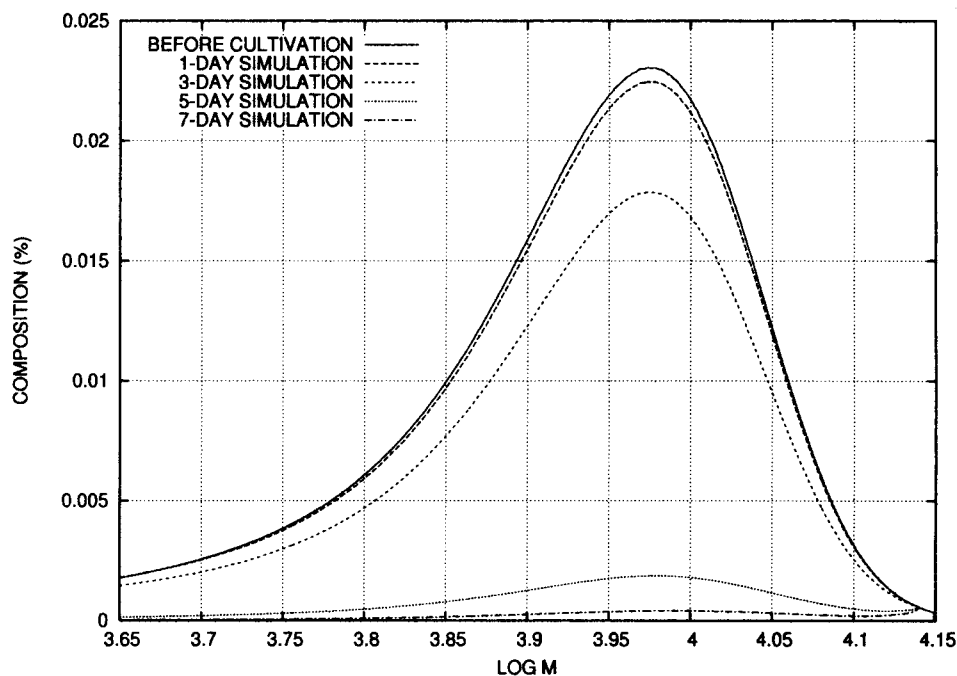


Figure 5: Transition of weight distribution for 7 days.

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