Simulation for microbial depolymerization processes of polyethylene glycol

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Abstract

Numerical techniques are applied to a set of experimental data to study depolymerization process of xenobiotic polymers. The molecular factor of the degradation rate is obtained numerically from the weight distribution before and after cultivation of microorganisms. The temporal factor of the degradation rate corresponds to the microbial population, and its essential parameters are determined numerically. The transition of the weight distribution is simulated by solving an initial value problem numerically. Numerical results are obtained for a microbial depolymerization process of polyethylene glycol.

Keywords: Biodegradation, Polymers, Polyethylene glycol, Mathematical model, Numerical simulation

1. Introduction

There are two types of microbial depolymerization processes, exogenous type and endogenous type. In exogenous type depolymerization processes, molecules are reduced by liberation of monomers from their terminals. A mathematical model was proposed and numerical techniques were developed to simulate exogenous depolymerization processes of polyethylene (PE) [1, 2]. Those techniques were also implemented to exogenous depolymerization processes of polyethylene glycol (PEG). The time dependence of degradation rates was taken into consideration in studies on depolymerization processes of PEG [3].

Molecules are cleaved by arbitrary scission in endogenous type depolymerization processes. A mathematical model was proposed and numerical techniques were developed to simulate the enzymatic degradation of polyvinyl alcohol (PVA) [11]. Those techniques were also applied to enzymatic hydrolysis of polylactic acid (PLA) [12]. A time factor of degradability was taken into consideration in a study of enzymatic hydrolysis of PLA [13].

The model proposed for endogenous type depolymerization processes was reformulated in studies on exogenous depolymerization processes of PEG, and PE [4]. Techniques developed for the PE biodegradation [4] were applied to exogenous depolymerization processes of PEG [5]. The time factor of the degradation rate was taken into consideration in studies on exogenous depolymerization processes of PEG [8, 9, 10].
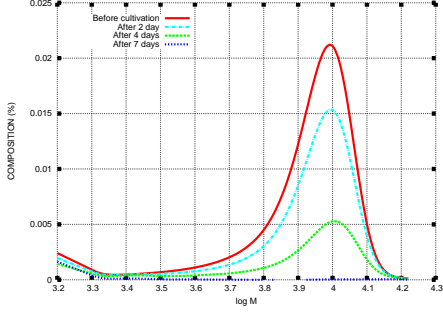
In this study, biodegradation of

Fig. 1: Weight distribution of PEG 6000 before and after cultivation of microbial consortium E1 for two days, four days, and seven days.

polyethylene glycol is revisited. Techniques developed previously are applied to another set of data shown in Figure 1. The mathematical model is described and numerical results are presented.

2. Mathematical model for exogenous type depolymerization processes

Molecules of a single polymer all have the same chemical structure, but their molecular weight varies from one molecule to another. Let t be the time and M be the molecular weight. Let $w(t, M)$ be the weight distribution of a polymer at time t, that is, the total weight of the molecules of molecular weight between A and B at time t is

$$\int_A^B w(t, M) \, dM.$$

Let $\gamma(t, M)$ be the loss in $w(t, M)$ per unit time and per unit weight, and $q(K, M)$ be the decrease in $w(t, M)$ per unit weight due to the transition of the weight from $w(t, M)$ to $w(t, K)$. Then $w(t, K)$ is a solution of the equation

$$\frac{\partial w}{\partial t} = -\gamma(t, M) w$$
$$+ \int_M^\infty u(t, M, K) w(t, K) \, dK, \tag{1}$$

where

$$u(t, M, K) = \frac{M}{K} \gamma(t, K) q(M, K).$$

Given an initial weight distribution $f(M)$, equation (1) and the initial condition

$$w(0, M) = f(M) \tag{2}$$

constitute an initial value problem, provided the degradation rate $\gamma(t, M)$ is known. Given an additional weight distribution $g(M)$ after the cultivation of microorganisms for some period T, equation (1), the initial condition (2), and the condition

$$w(T, M) = g(M) \tag{3}$$

constitute an inverse problem for the degradation rate $\gamma(t, M)$, for which the solution of the initial value problem (1) and (2) also satisfies the condition (3).

Time factors of degradability such as temperature, dissolved oxygen, and microbial population act evenly on molecules regardless of molecular weight, and the degradation rate $\gamma(t, M)$ is a product of a function of t, which we call $\sigma(t)$, and a function of M, which we call $\lambda(M)$. Substitution of $\gamma(t, M) = \sigma(t) \lambda(M)$ in equation (1) leads to

$$\frac{\partial w}{\partial t} = \sigma(t) \left[-\lambda(M) w \right.$$
$$\left. + \int_M^\infty v(M, K) w(t, K) \, dK \right] \tag{4}$$

where

$$v(M, K) = \frac{M}{K} \lambda(K) q(M, K).$$

In an exogenous depolymerization process, $q(K, M)$ is given by

$$q(K, M) = \rho e^{-\rho(M-K)}.$$

Equation (4) becomes

$$\frac{\partial w}{\partial t} = \sigma(t) \left[-\lambda(M) w \right.$$
$$\left. + \int_M^\infty c(M) d(K) w(t, K) \, dK \right]$$
$$\tag{5}$$

where

$$c(M) = \rho M e^{\rho M}, \qquad d(K) = \frac{1}{K} e^{-\rho K}.$$
$$\tag{6}$$

The value of the the parameter ρ, which is called the intensity of the exponential distribution, is given by

$$\rho = \frac{\log 2}{L}, \tag{7}$$

where L is the molecular weight of a monomer (PE: $L = 28$, CH_2CH_2, PEG: $L = 44$, CH_2CH_2O) [4, 5, 6].

The results shown in Figure 1 were obtained in experiments in which the only time factor was the microbial population. A mathematical model for the transition of microbial population was proposed in a previous study [3]. Truncated monomers from the terminals of molecules were the carbon source for the microorganisms, and their total amount at time t is

$$A(t) = \int_0^\infty \sigma(t) \lambda(M) w(t, M) \, dM.$$

Let h be the amount per unit population for which the microbial population is stationary. The microbial population $\sigma(t)$ increases over a period in which $h < A(t)$, and decreases over a period in which $h > A(t)$. The growth rate of the microbial population is

$$k \left(1 - h \frac{\sigma(t)}{A(t)} \right), \tag{8}$$

where k is a positive constant. The microbial population $\sigma(t)$ satisfies

$$\frac{d\sigma}{dt} = \left(1 - h \frac{\sigma(t)}{A(t)} \right) \sigma. \tag{9}$$

Equation (9) is associated with the initial condition

$$\sigma(M) = \sigma_0, \tag{10}$$

where σ_0 is the initial microbial population.

3. Inverse problem for the time factor of the degradation rate

Define τ by

$$\tau = \int_0^t \sigma(s) \, ds \tag{11}$$

and let $W(\tau, M) = w(t, M)$. Equation (5) leads to

$$\frac{\partial W}{\partial t} = -\lambda(M) W$$
$$+ \int_M^\infty c(M) d(K) W(\tau, K) \, dK.$$
$$\tag{12}$$

Equation (12) and the initial condition

$$W(0, M) = f(M) \tag{13}$$

constitute an initial value problem, provided the molecular factor of the degradation rate $\lambda(M)$ is given. Equation (12), the initial condition (13) and the condition

$$W(\mathcal{T}, M) = g(M) \tag{14}$$

constitute an inverse problem for the molecular factor $\lambda(M)$ for which the solution of the initial value problem (12) and (13) also satisfies the condition (14). The initial value problem (1) and (2) corresponds to the initial value problem (12) and (13), and the inverse
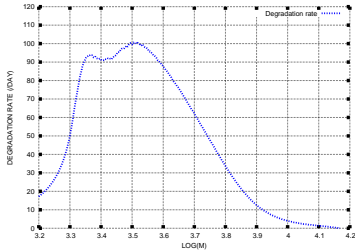
Fig. 2: Degradation rate based on the weight distributions before and after cultivation of the microbial consortium E1 on PEG 6000 for two days.

Fig. 3: Numerical solution of the initial value problem (12) and (13). The experimental results for $t = 2$, $t = 4$, and $t = 7$ are also shown.

problem (1), (2) and (3) corresponds to the inverse problem (12), (13) and (14).

The weight distributions before and after cultivation for two days (Figure 1) were set as the initial and final weight distributions, respectively, and functions $c(M)$ and $d(K)$ were set as given by the expressions (6) and (7). Techniques developed in previous studies ([4, 5]) were used to solve the inverse problem (12), (13) and (14) for the molecular factor of the degradation rate $\lambda(M)$, for which the solution of the initial value problem (12) and (13) also satisfies the condition (14). Figure 2 shows a numerical result. Figure 3 shows the profiles of a numerical solution of the initial value problem (12) and (13) at $\tau = 2$, $\tau = 10$, and $\tau = 52$, which correspond to the experimental results for $t = 2$, $t = 4$, and $t = 7$, respectively.

4. Depolymerization process of PEG 6000

System of equations (4) and (9) subject to the initial conditions (2) and (10) was solved numerically for another set of data for various values of parameters
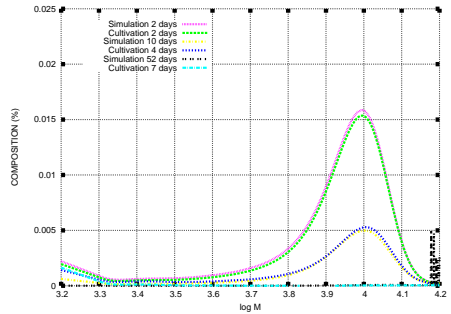
[7, 8, 9, 10, 14]. If $S(\tau) = \sigma(t)$, $S(\tau)$ is the solution of the initial value problem

$$\frac{dS}{d\tau} = k\left(1 - h\frac{1}{\int_0^\infty \lambda(M)\,W(\tau,\,M)\,dM}\right),$$
(15)
$$S(0) = \sigma_0, \qquad (16)$$

in view of the definition (11), and

$$t = q(\tau) = \int_0^\tau \frac{1}{S(r)}\,dr \qquad (17)$$

holds. Let

$$f_i(\sigma_0, k, h) = t_i - q(\tau_i) \qquad (i = 1, 2, 3),$$

where $t_1 = 2$, $t_2 = 4$, $t_3 = 7$, $\tau_1 = 2$, $\tau_2 = 10$, and $\tau_3 = 52$ according to the result shown in Figure 3. The Newton-Raphson method was implemented to determine the value of parameters σ_0, k, and h for which

$$f_i(\sigma_0, k, h) = 0 \ (i = 1, 2, 3) \qquad (18)$$

for another set of data [14]. Values of the parameters are generated with the Newton-Raphson method. The initial values

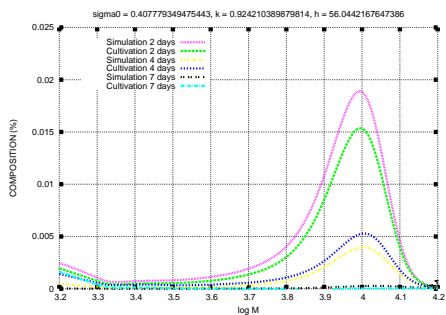$$\sigma_0^{(0)} = 0.46,\ k^{(0)} = 0.74,\ h^{(0)} = 97.0.$$

Fig. 4: A numerical result for the transition of the weight distribution. Experimental results are also shown.

were set, and the values of the parameters

$$\sigma_0 \approx 040778,\ k \approx 0.92421,$$

$$h \approx 56.0442$$

were obtained after forty two iterations, where the residual in the consecutive approximations was approximately 0.7632. System of equations (4) and (9) subject to the initial conditions (2) and (10) were solved numerically for those values of the parameters. Figure 4 shows the numerical result.

5. Conclusion

Numerical techniques developed in previous study were applied to simulate the transition of the weight distribution of PEG 6000. Numerical result shows that the techniques are applicable to a wide range of exogenous depolymerization processes.

Acknowledgment

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