Computational analysis for biodegradation of exogenously depolymerizable polymer

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Abstract. This study shows that microbial growth and decay in a biodegradation process of exogenously depolymerizable polymer are controlled by consumption of monomer units. Experimental outcomes for residual polymer were incorporated in inverse analysis for a degradation rate. The Gauss-Newton method was applied to an inverse problem for two parameter values associated with the microbial population. A biodegradation process of polyethylene glycol was analyzed numerically, and numerical outcomes were obtained.

1. Introduction

A large amount of synthetic polymers have been produced since around med twentieth century. Those macromolecules would be nonexistent unless they were invented. However, some of those xenobiotic compounds are utilizable by microorganisms. Those synthetic materials have been accumulated, and they have become possible sources for carbon dioxide emission. So polymeric biodegradation should throughly be studied. There are two types of processes in polymeric biodegradation. The molecular reduction by terminal liberation of monomer units is the primary factor of a depolymerization process of exogenous type. Polyethylene (PE) and polyethylene glycol (PEG) are exogenously depolymerizable polymers. A mathematical model was formulated and numerical techniques were developed for PE biodegradation [1]. Those mathematical techniques were implemented in analyses of biodegradation processes of PEG [2]. A time-dependent degradation rate was considered in formulation of a PEG depolymerization process [3].

Unlike exogenously depolymerizable polymers, molecules of endogenously depolymerizable polymers break down randomly. Polyvinyl alcohol (PVA) and polylactic acid (PLA) are endogenously depolymerizable polymers. A mathematical model was proposed and numerical techniques were developed for an enzymatic degradation process of PVA [4]. Those techniques were implemented in a study of enzymatic hydrolysis of PLA, and outcomes for PVA and PLA were compared [5]. A time-dependent degradation rate was considered in formulatoin of an enzymatic hydrolysis of PLA [6]. A techniques developed for endogenously depolymerizable polymers were implemented in studies of exogenous type depolymerization processes of PEG [7] and PE [8]. Mathematical techniques for the PE biodegradation were implemented in study of PEG biodegradation processes [9]. A time-dependent degradation rate was considered in formulation of a PEG depolymerization process [10].

This study revisited a depolymerization process of PEG. In the following sections, mathematical model is described, numerical techniques used in an inverse analysis for a time factor of a degradation rate are illustrated, and numerical outcomes are introduced.

2. Mathematical formulation for exogenously depolymerizable polymers

Consider a microbial depolymerization process in a culture medium. Let M be the molecular weight, and let t be the time. Denote the weight distribution with respect to M at t by $w(t, M)$ [mg], and the residual of polymer consisting of molecules with molecular weight between A and B at time t by $v(t)$ [mg]. The residual $v(t)$ is expressed by the integral of $w(t, M)$ with respect to M,

$$v(t) = \int_A^B w(t, M)\, dM . \tag{1}$$

In particular, total weight $v(t)$ of the entire residual polymer at time t is expressed by

$$v(t) = \int_0^\infty w(t, M)\, dM . \tag{2}$$

Integral (1) is an appropriate approximation of integral (2) for suitable values of A and B.

Denote the population of viable microorganisms at time t by $\sigma(t)$. Equation

$$\frac{\partial w}{\partial t} = \sigma(t) \left[-\lambda(M)w + c(M) \int_M^\infty \lambda(K) d(K) w(t, K)\, dK \right] \quad \left(c(M) = M e^{\rho M}, \; d(M) = \frac{e^{-\rho M}}{M(1 - e^{-\rho M})}, \; \rho = \frac{\log 2}{L} \right) \tag{3}$$

was previously proposed [9 - 14]. Parameter L denotes the molecular weight of a monomer unit, *e.g.* PE: $L = 28$ (CH_2CH_2), PEG: $L = 44$ (CH_2CH_2O). The degradation rate per unit time, unit weight, and unit population was decomposed into a molecular factor and a time factor. Function $\lambda(M)$ denotes the molecular factor, whereas the microbial population $\sigma(t)$ is the time factor. Equations (2) lead to

$$v'(t) = \sigma(t) \int_0^M \left[-\lambda(M)w + c(M) \int_M^\infty \lambda(K) d(K) w(t, K)\, dK \right] dM .$$

In a previous study, equation

$$\frac{d\sigma}{dt} = k \left[1 - h \frac{\sigma}{u(t)} \right], \tag{4}$$

was proposed for the microbial population, where $u(t) = -v'(t)$. In this study, equation (4) was replaced by

$$\frac{d\sigma}{dt} = ku(t) - h\sigma. \tag{5}$$

The term $ku(t)$ is the conversion of consumption of monomer units, and the term $-h\sigma$ is the reduction by viability loss. Suppose that $f_0(M)$ is an initial weight distribution, and that σ_0 is an initial population of viable microorganisms. system of equations (3), (5) and initial conditions $w(0, M) = f_0(M)$, $\sigma(0) = \sigma_0$ constitute an initial value problem.

3. Numerical results for inverse analysis of microbial population

The initial value problem associated with equations (3) and (5) is solvable for $w(t, M)$ and $\sigma(t)$ provided that the function $\lambda(M)$ is given and that values of parameters σ_0, k, and h are prescribed. To specify the function $\lambda(M)$ and values of parameters σ_0, k, and h, consider change of variables

$$\tau = \int_0^t \sigma(s)\, ds. \tag{6}$$

Denote $w(t, M)$, $\sigma(t)$, and $v(t)$ by $W(\tau, M)$, $S(\tau)$, and $V(\tau)$, respectively. Equations

$$\frac{\partial W}{\partial \tau} = -\lambda(M)W + c(M)\int_M^\infty \lambda(K)d(K)W(\tau, K)\,dK\,, \qquad (7)$$

$$\frac{dS}{d\tau} = kU(\tau) - h, \qquad\qquad (U(\tau) = -V'(\tau)) \qquad (8)$$

are derived from the equations (3) and (5), respectively. Note that the following equations hold.

$$V(\tau) = \int_0^\infty W(\tau, M)\,dM\,, \qquad V'(\tau) = \int_0^M \left[-\lambda(M)W + c(M)\int_M^\infty \lambda(K)d(K)W(\tau, K)\,dK\right]dM\,.$$

Suppose that $F_1(M)$ and $F_2(M)$ are weight distributions for $\tau = T_1$ and $\tau = T_2$ $(0 \le T_1 < T_2)$, respectively, equation (8) and conditions $W(T_1, M) = F_1(M)$, $W(T_2, M) = F_2(M)$ constitute an inverse problem for $\lambda(M)$ such that the solution of equation (7) satisfies those conditions.

Numerical techniques for the inverse problem were previously developed. Suppose that weight distributions $f_0(M)$, $f_1(M)$, ..., $f_m(M)$ for t_0, t_1, ..., t_m, respectively, are given, so   that $w(t_0, M) = f_0(M)$, $w(t_1, M) = f_1(M)$, ..., $w(t_m, M) = f_m(M)$. A pair of weight distributions were assigned to the functions $F_1(M)$ and $F_2(M)$, and the inverse problem for $\lambda(M)$ was obtained numerically. Once $\lambda(M)$ was specified, equation (7) was solved for $W(\tau, M)$ with condition $W(0, M) = f_0(M)$. Once $W(\tau, M)$ was obtained, equations $V(\tau_i) = v(t_i)$ $(i = 0, 1, \ldots, m)$ were solved numerically, and values of τ_i $(i = 0, 1, \ldots, m)$ were obtained. Previous studies show that an exponential function $e^{-\mu\tau}$ approximates $V(\tau)$ with an appropriate value of μ. In this study, value $\mu = 0.1$ was set.

Suppose that $S(\tau, \sigma_0, k, h)$ is the solution of equation (8) with condition $S(0, \sigma_0, k, h) = \sigma_0$. Note that $S(\tau, \sigma_0, k, h) = \sigma_0 + k[v_0 - V(\tau)] - h\tau$, where $v_0 = V(0)$. The change of variables (6) leads to the equation $t = q(\tau, \sigma_0, k, h)$, where

$$q(\tau, \sigma_0, k, h) = \int_0^\tau \frac{dr}{S(r, \sigma_0, k, h)}\,. \qquad (9)$$

Given m pairs of values of t and τ, (t_i, τ_i) $(i = 1, 2, \ldots, m)$, define functions $g_i(\sigma_0, k, h)$ $(i = 1, 2, \ldots, m)$ by $g_i(\sigma_0, k, h) = q(\tau_i, \sigma_0, k, h) - t_i$, and consider the system of equations for σ_0, k, and h,

$$g_i(\sigma_0, k, h) = 0 \quad (i = 1, 2, \ldots, m). \qquad (10)$$

Values of residual PEG v_i at $t_i = i$ $(i = 0, 1, 2, \ldots, 6)$ (day), and v_7, and v_8 at 8 and 10 days, respectively, were reported [16]. In a previous study, some of those values were incorporated into analysis of an inverse problem derived from equation (4) [16]. Some of those values v_i $(i = 0, 1, 2, \ldots, 6)$ were also introduced into an inverse analysis in this study. Initial microbial

population σ_0 was fixed ($\sigma_0 = 1.0$), and the Gauss-Newton method was applied to the least square problem for

$$\frac{1}{2}\sum_{i=1}^{5}\left[g_i(\sigma_0, k, h)\right]^2 . \qquad (11)$$

With initial values $k = 0.1$ and $h = 2.0$, residuals $\left(\sqrt{(k_n - k_{n-1})^2 + (h_n - h_{n-1})^2}\right)$ between two successive approximations was reduced to a value that was less than 10^{-15} after fourteen iterations. Those final values are $k = 0.04934293\,62357295$ and $h = 1.01446006\,075672$. The graphs of the residual PEG $(t, v(t)) = (q(\tau, \sigma_0, k, h), V(\tau))$ and the microbial population $(t, \sigma(t)) = (q(\tau, \sigma_0, k, h), S(\tau, \sigma_0, k, h))$ were generated numerically for those values of k and h. Values of the microbial density [10^9/ml] (*S. terrae*) were obtained experimentally [14]. Those values and values of $\sigma(t) = S(\tau, \sigma_0, k, h)$ $(t = q(\tau, \sigma_0, k, h))$ were compared, and a linear conversion of $(t, \sigma(t)) = (q(\tau, \sigma_0, k, h), S(\tau, \sigma_0, k, h))$ according to a least square approximation is shown (Figure 2).

4. Conclusion

In previous studies [10 – 13], experimental outcomes before and after cultivation of microorganisms in culture media were incorporated into inverse analysis for $\lambda(M)$ and $\sigma(t)$. A recent study [16] demonstrated that an exogenous type microbial depolymerization process can be simulated with a set of residual polymer before after cultivation of microorganisms. The Gauss-Newton method [16] was applied to a nonlinear least square problem derived from the an equation for the microbial population. In this study, the Gauss-Newton method was applied to the square sum (11).

The symbiotic mixed culture E-1 consists of *S. terrae* and *Rhizobium* sp., and *S. terrae* was a primary PEG utilizing bacteria. The viable cell density of *S. terrae* was measured by colony counting [15]. Figure 3 (b) shows the transition of viable cell density of *S. terrae* and a conversion of the numerical result for the microbial population. Figure 2 (b) shows a notable disagreement between experimental results and numerical results for $3 \le t \le 6$.
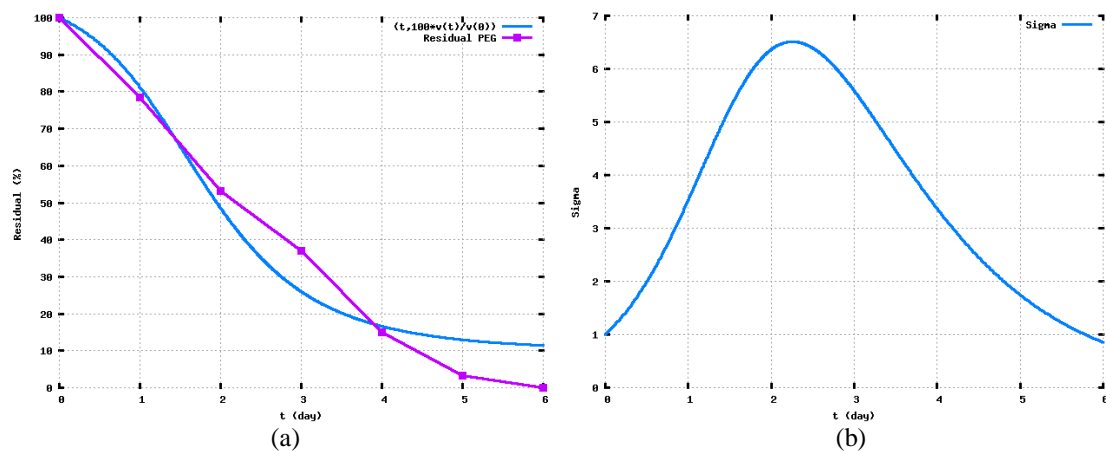
Figure 1. (a) Residual PEG $(t, v(t)) = (q(\tau, \sigma_0, k, h), V(\tau))$. Experimental results [16] are also shown. (b) Microbial population $(t, \sigma(t)) = (q(\tau, \sigma_0, k, h), S(\tau, \sigma_0, k, h))$. Those curves were generated numerically for the values of σ_0, k, and h, $\sigma_0 = 1.0$, $k = 0.04934293\,62357295$, and $h = 1.01446006\,075672$.
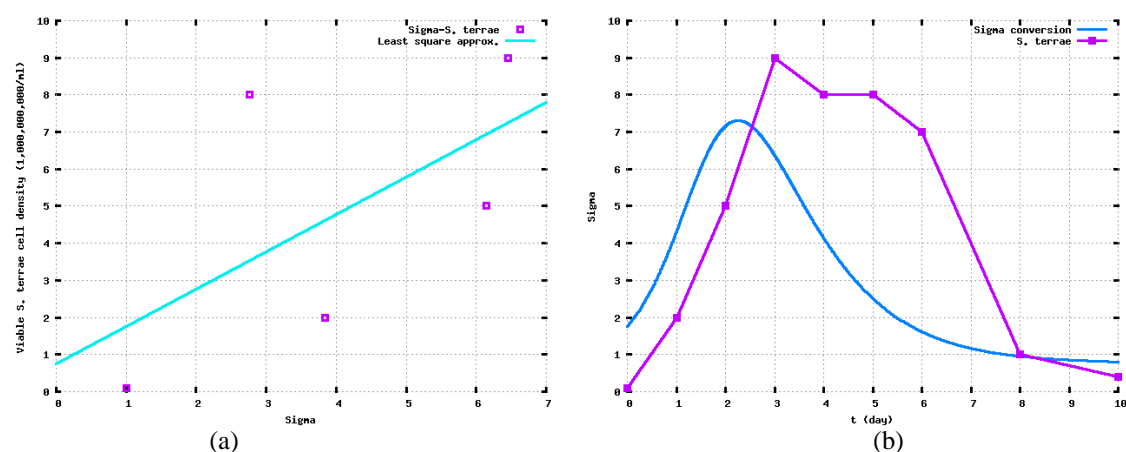

Figure 2. (a) Values of the microbial density [10^9 /ml] of *S. terrae* and values of $\sigma(t) = S(\tau, \sigma_0, k, h)$ $(t = q(\tau, \sigma_0, k, h))$ (b) linear conversion of $(t, \sigma(t)) = (q(\tau, \sigma_0, k, h), S(\tau, \sigma_0, k, h))$ according to a least square approximation

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