A simplified mathematical model to predict PVC photodegradation in photobioreactors

C.A. D’Aquino a,b,*, W. Balmant a, R.L.L. Ribeiro a,b, M. Munaro c, J.V.C. Vargas a,b, S.C. Amico d

a Núcleo de Pesquisa e Desenvolvimento em Energia Auto-Sustentável, UFPR – Universidade Federal do Paraná, CP 19011, 81531-980 Curitiba, PR, Brazil
b Programa de Pós-graduação em Engenharia e Ciência dos Materiais, PIPE, UFPR – Universidade Federal do Paraná, CP 19011, 81531-980 Curitiba, PR, Brazil
c Instituto de Tecnologia para o Desenvolvimento, LACTEC, Centro Politécnico da UFPR, CP 19067, 81531-980 Curitiba, PR, Brazil
d Departamento de Engenharia dos Materiais, UFRGS – Universidade Federal do Rio Grande do Sul, Av. Bento Gonçalves, 9500, CEP 91501-970, Porto Alegre, RS, Brazil

Abstract

A simplified mathematical model to predict transparent poly(vinyl chloride) (PVC) degradation in photobioreactors under the incidence of sunlight is proposed. The model is based on the widely accepted theory of photochemistry degradation, which states that HCl is produced as an intermediate compound yielded in a propagation reaction, taking into account the entire dehydrochlorination process. A system of ordinary differential equations for concentrations and energy with respect to time results from the application of the principles of species and energy conservation, which is integrated explicitly and accurately with low computational time. Previously published experimental data were used to validate the numerical simulation results obtained with the model, with good quantitative and qualitative agreement. The developed model is expected to be a useful tool for simulation, design, and optimization of PVC for minimum photodegradation.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Photobioreactors are systems that offer better control over microalgae cultivation conditions and growth parameters than open ponds. Closed reactors are made of glass or plastic to allow for outdoor sunlight exposure for photosynthesis, allowing cost reduction of microalgae production and, consequently, their products [1,2].

The materials used in the photobioreactor construction must be nontoxic, show high transparency, high mechanical strength and durability, chemical stability and low cost [3]. Because of this, the most commonly used materials are acrylic, polycarbonate, low-density polyethylene and crystal PVC (poly(vinyl chloride)) [4]. PVC presents the advantage of low cost, long-term stability and flame resistance in comparison to other commodity plastics, and its mechanical properties may be controlled by varying the amount of plasticizer [5].

The selection of any polymer for this application is highly dependent on the maintenance of the optical and mechanical properties after long periods of sun exposure. In outdoor applications, polymers degrade because of a combination of several environmental factors (especially sunlight intensity, temperature and humidity), and the rate of degradation varies according to the polymer structure and formulation, and the production process [6]. PVC in particular may contain structural defects caused by its processing, resulting in the dehydrochlorination process, whose reaction steps are depicted in Fig. 1. The defects in the PVC molecules (e.g. long and short chain branches, terminal and internal unsaturation, unusual end groups, both initiator and emulsifier residues) [7] make the molecules absorb wavelengths in the UV region which cause its photodegradation, resulting in a yellowness effect [8,9].
Although the mechanism by which that happens is well known, the effect on the polymer lifetime is still controversial, especially when light is among the leading degradation factors. Studies on natural and accelerated degradation may be found in the literature [10–12] and they usually try to understand the process by using traditional physical-chemical characterization techniques, such as differential scanning calorimetry (DSC), spectroscopy, thermal-mechanical analysis. Even though such techniques are important tools to understand polymer behaviour under different conditions, they demand a long time to estimate polymer lifetime.

Mathematical modelling of the polymer aging process may be an important tool, not only to predict lifetime of a certain polymer, but also to understand the complex processes and parameters that affect polymer degradation. With respect to PVC degradation, its zip dehydrochlorination may be considered a complex process due to the production of intermediate compounds that extensively affect the model parameters, which makes the lifetime prediction inaccurate. Bystritskaya et al. [13] developed a theoretical model based on a relationship between material properties and aging conditions with some unknown parameters with regression dependence. They obtained, in Arrhenius terms, a Bayesian distribution in which it is possible to have a satisfactory polymer lifetime prediction.

Other authors suggested the inclusion of the radical effect in their models, since the produced radicals accelerate degradation [14,15]. In these references, a population balance equation is derived to predict degradation of poly(methyl methacrylate) (PMMA) and polyethylene, producing interesting results but for non-isothermal data.

Sánchez-Jiménez et al. [16] proposed a model to predict PVC degradation considering two distinct dehydrochlorination processes involving nucleation, growth and diffusion mechanisms. The model was developed based on the Arrhenius law that describes the reaction rate in the solid state. The obtained results satisfactorily captured the correlation between kinetics of the thermal dehydrochlorination of PVC and its macromolecule structure, even though they considered temperatures above 450 K, which are not achievable under natural circumstances. These authors included an additional factor in the reaction rate calculation, \( f(\tau) \), which is obtained through algebraic functions describing polymer degradation kinetics. Based on this new mathematical formulation, various authors inferred that the degradation rate is not constant [13,17], especially in the PVC case, due to dehydrochlorination. For instance, Celina et al. [17] used a non-Arrhenius behaviour model to introduce changes in degradation rate due to subreactions that occur during the process. Their model proposed the utilization of two competing reactions with individual temperature dependence.

Based on the literature review, mathematical models for polymer aging prediction are still needed. Extending transparent PVC lifetime for photobioreactor applications may be associated with global environmental preservation aspects. For instance, the biodiesel derived microalgae cultivation photobioreactor shown in Fig. 2 is used for sustainable energy production [2] and is built with transparent PVC pipes. Therefore, the objective of this paper is to introduce a novel mathematical model to predict poly(vinyl chloride) degradation in photobioreactors under the incidence of sunlight. The model considers that the radicals produced during the initial PVC degradation will accumulate in the system until a sufficient concentration of radicals that is able to accelerate degradation is reached. In order to represent the accumulation of HCl molecules, a cooperative system was considered, as suggested by Singh et al. [18].

<table>
<thead>
<tr>
<th>List of symbols</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A</strong> pre-exponential factor, s(^{-1})</td>
</tr>
<tr>
<td><strong>[Cl]</strong> concentration of chlorine radical on PVC, mol L(^{-1})</td>
</tr>
<tr>
<td><strong>E</strong> energy, J</td>
</tr>
<tr>
<td><strong>[HCl]</strong> concentration of hydrochloric acid on PVC, mol L(^{-1})</td>
</tr>
<tr>
<td><strong>I(_{0})</strong> incident sun light irradiation on PVC surface, W m(^{-2})</td>
</tr>
<tr>
<td><strong>I(_{s})</strong> sun light irradiation not absorbed by PVC surface, W m(^{-2})</td>
</tr>
<tr>
<td><strong>k(_{1})</strong> reaction rate of PVC degradation, s(^{-1})</td>
</tr>
<tr>
<td><strong>k(_{2})</strong> reaction rate of HCl production, L mol(^{-1}) s(^{-1})</td>
</tr>
<tr>
<td><strong>k(_{i})</strong> inverse reaction rate of HCl production, L mol(^{-1}) s(^{-1})</td>
</tr>
<tr>
<td><strong>I</strong> thickness of PVC film sample, cm</td>
</tr>
<tr>
<td><strong>n</strong> Hill coefficient</td>
</tr>
<tr>
<td><strong>[PVC]</strong> concentration of PVC, mol L(^{-1})</td>
</tr>
<tr>
<td><strong>[PVC]</strong> concentration of PVC radical, mol L(^{-1})</td>
</tr>
<tr>
<td>( \sim \text{CH}_2\text{CH}_2 \sim ) concentration of degraded PVC, mol L(^{-1})</td>
</tr>
<tr>
<td><strong>R</strong> ideal gas constant, L atm K(^{-1}) mol(^{-1})</td>
</tr>
<tr>
<td><strong>S</strong> half saturation constant of Hill equation, J</td>
</tr>
<tr>
<td><strong>t</strong> time, s</td>
</tr>
<tr>
<td><strong>T</strong> temperature, K</td>
</tr>
<tr>
<td><strong>Y</strong> yield coefficient of chemical energy to PVC degradation, J mol(^{-1})</td>
</tr>
</tbody>
</table>

**Greek letters**

| **\( \alpha \)** molar absorptivity, L mol\(^{-1}\) cm\(^{-1}\) |
| **\( \Delta Y_{0} \)** PVC yellowing percent, % |

**Subscripts**

| **a** activation |
| **CV** control volume |
| light luminous |
| **q** chemical |
| **qabs** absorbed chemical energy |
| **0** initial condition |

2. Mathematical model

2.1. Balance of chemical species

According to the reaction presented in Fig. 1, an ionic mechanism equation was considered, as suggested by
Starnes [19], in which the produced radical (i.e. chlorine) is responsible for a transfer process that generates new defects and leads to auto-acceleration, according to the following reaction:

\[
PVC + Cl \xrightarrow{k_1} Cl^* \\
\xrightarrow{k_2} \sim CH_2CH_2 \sim + 2HCl
\]  

(1)

The rate of product generation related to each equation depends on the reaction constants \( k_1 \) and \( k_2 \), the initial luminous irradiation \( (I_0) \) and the constant of reverse reaction \( (k_i) \) at a lower rate, once \( k_i \ll k_2 \). Based on species conservation, the consumption of chemical species is estimated according to the following equations:

\[
\frac{d[HCl]}{dt} = k_2 \cdot [PVC] \cdot [Cl^*] - k_1 \cdot [\sim CH_2CH_2 \sim] \cdot [HCl]
\]  

(2)

\[
\frac{d[\sim CH_2CH_2 \sim]}{dt} = k_2 \cdot [PVC] \cdot [Cl^*] - k_1 \cdot [\sim CH_2CH_2 \sim] \cdot [HCl]
\]  

(3)

\[
\frac{d[Cl^*]}{dt} = k_1 \cdot [PVC] - k_2 \cdot [PVC^*] \cdot [Cl^*] + k_1 \cdot [\sim CH_2CH_2 \sim] \cdot [HCl]
\]  

(4)

\[
\frac{d[PVC^*]}{dt} = k_1 \cdot [PVC] - k_2 \cdot [PVC^*] \cdot [Cl^*] + k_1 \cdot [\sim CH_2CH_2 \sim] \cdot [HCl]
\]  

(5)

As shown in Eq. (1), the degradation of PVC results in HCl generation. Therefore, it is possible to obtain a first order process with respect to the non-degraded polymer mass, and the reaction constant, \( k_1 \), as follows:

\[
\frac{d[PVC]}{dt} = -k_1 \cdot [PVC]
\]  

(6)

The constant \( k_1 \) is the degradation rate, which can be obtained based on the Arrhenius extrapolation:

\[
k_1 = A \cdot \exp \left( -\frac{E_a}{R \cdot T} \right)
\]  

(7)

where \( k_1 \) is the reaction rate, \( A \) is the Arrhenius pre-exponential factor, \( R \) is the ideal gas constant, \( E_a \) is the activation energy and \( T \) is the process temperature.

However, Eq. (7) is insufficient to portray the complex reactions that occur during PVC degradation [17,20]. The coefficient \( k_1 \) cannot capture the actual reaction production, since it disregards the change in degradation rate that takes place throughout the process [16,17]. Such changes
result in a sigmoidal kinetics, as shown by Real and Gardette [21]. In nature, the same profile is observed in single-substrate enzymatic reactions, in other words, the polymeric structures in biochemical systems [22]. A cooperation mechanism is observed in such systems, where the degradation rate is influenced by the intermediate compounds and their effects on the system. An equation that captures such behaviour in biochemical systems is the Hill equation [23]. This equation introduces the chemical energy theory, i.e. the energy content of each molecule, which states that for all energy that enters a system, some of it will be transmitted, some will be reflected and just the amount supported by the bond will be absorbed.

In the case of PVC degradation, the cooperative process occurs when light is absorbed by PVC as chemical energy in different steps: a) in the region of low chemical energy, the reaction occurs at low rate; b) as chemical energy accumulates in the system (i.e. increasing concentration), the reaction progresses at higher rates. Based on the observation of this phenomenon, this work proposes a model that considers the accumulation of energy in chemical bonds as chemical energy (Eq.). Therefore, the degradation coefficient is now determined as follows:

\[
k_1 = A \exp \left( \frac{E_x}{R \cdot T} \right) \frac{E_q^2}{S^2} \tag{8}\]

where \( A \) is the Hill coefficient and \( S \) is the half saturation constant in the Hill equation. This equation is adequate for representing the degradation kinetics since the chemical energy dependence is written in terms of the absorbed luminous energy and the specific material characteristics in the energy balance of the system.

Finally, in order to assess PVC degradation over time, and assuming the yellowing is caused by HCl, the PVC yellowing percent in this model is defined as follows:

\[
\Delta Y^\circ = \left( \frac{[\text{HCl}]}{[\text{PVC}]_0} \right) \times 100 \tag{9}\]

2.2. Energy balance

Taking, for example, as a control volume, a thin film sample of the transparent PVC pipes shown in Fig. 2, the sunlight energy enters the control volume and is divided into chemical energy in the molecular bonds and luminous energy, so that the total energy accumulation/dissipation rate in the control volume may be written as:

\[
\frac{dE_{\text{cv}}}{dt} = \frac{dE_q}{dt} + \frac{dE_{\text{light}}}{dt} \equiv \frac{dE_q}{dt} \tag{10}\]

assuming that the luminous energy accumulation rate is negligible in the presence of the chemical energy accumulation rate in the molecular bonds.

The luminous irradiation that leaves the control volume \( (I_a) \) is given by the Lambert–Beer law as follows [23]:

\[
I_a = I_0 \cdot e^{-\alpha \cdot t \cdot [\text{PVC}]} \tag{11}\]

where \( \alpha \) is the absorption coefficient and \( t \) the thickness of the PVC sample. The \( I_0 \) dependence on thickness is considered important by several authors since different effects are observed for wavelengths lower than 100 \( \mu \text{m} \), within 100 and 400 \( \mu \text{m} \), and beyond 400 \( \mu \text{m} \) [24].

The control volume chemical energy balance therefore states that:

\[
\frac{dE_q}{dt} = \dot{E}_{\text{qabs}} - Y \cdot k_1 \cdot [\text{PVC}] \tag{12}\]

The energy balance considers that the absorbed chemical energy in the control volume will be either consumed during PVC degradation, which is dependent on the yield coefficient of chemical energy to PVC degradation \( (Y) \), or will accumulate in the system. The absorbed chemical energy by the control volume is the difference between the sun irradiation that hits and leaves the PVC, calculated using Eq. (11):

\[
\dot{E}_{\text{qabs}} = I_0 - I_a = I_0 \cdot (1 - e^{-\alpha \cdot t \cdot [\text{PVC}]}) \tag{13}\]

3. Numerical method

Eqs. (2)–(6) and (12) define a system of six ordinary differential equations that was integrated numerically with an adaptive time step fourth-fifth order Runge-Kutta method [25], together with Eqs. (8), (10), and (12), in which the local truncation error was kept below a pre-specified tolerance \( 10^{-6} \). The integration started from given initial conditions \([\text{HCl}], [\text{~CH}_2\text{CH}_2\text{~}], [\text{C}^\circ], [\text{PVC}], [\text{PVC}], E_q(0) = 0 \text{ mol L}^{-1}, 0 \text{ mol L}^{-1}, 0 \text{ mol L}^{-1}, 22.5 \text{ mol L}^{-1}, 0 \text{ J}_0\), until a pre-specified 2000 h final simulation time was achieved, which corresponds to the standard value used to test PVC resistance to light [26]. The objective was to monitor the production and consumption of chemical species involved in the reaction shown in Fig. 1 and the variation of the chemical energy of the system during PVC degradation.

4. Results and discussion

The parameters used in the mathematical model to perform the simulations are listed in Table 1. The activation energy, temperature and light irradiation values were taken from Real and Gardette experiments [21, 26], who monitored polymer degradation by colorimetric determinations. These authors analyzed PVC degradation focusing on two different formulations containing a benzotriazole anti-UV additive: PVC1 (with a thermal stabilizer based on Ca/Zn) and PVC3 (with a thermal stabilizer based on Sn). Both PVC samples will be analysed here. In order to express the data in terms of PVC yellowing percent \( (\Delta Y^\circ) \), the yellowness dependence on HCl emission kinetics has been established as recommended by Krongauz et al. [27], which resulted in the formulation proposed in Eq. (9).

A sigmoidal profile is observed in the consumption/production of all chemical species in the medium in all computational simulations performed with the model, as shown in Figs. 3–6. Fig. 3 shows the evolution of [HCl] with respect to time for the entire duration of the 2000 h resistance to light test for the PVC1 sample. The model was able to capture the initial delay in the degradation process, the subsequent increase in degradation rate and the final
stabilization trend, as described above, therefore being consistent with the physical phenomenon. Similarly, Fig. 4 displays the \[\text{[HCl]}\] simulation results for the PVC3 sample. Direct comparison between Figs. 3 and 4 shows that the PVC1 sample upon stabilization reaches a significantly higher level of degradation than the PVC3 sample (\[\text{[HCl]}_{\text{PVC1}} = 10.5 \text{ mol L}^{-1} \text{ and } \text{[HCl]}_{\text{PVC3}} = 8 \text{ mol L}^{-1}\)), roughly 30% higher.

Figs. 5 and 6 depict the \[\text{[PVC1]}\] and \[\text{[PVC3]}\] with respect to time for the entire simulation period, respectively. It is observed that, although both samples show that \[\text{[PVC]} \rightarrow 0\] at the end of the simulation time, \[\text{[PVC1]}\] starts to drop earlier than \[\text{[PVC3]}\]. Therefore, the combined observation of Figs. 3–6 indicates that the PVC3 sample (containing Sn stabilizer) is expected to show better performance with respect to degradation than PVC1 (containing Ca/Zn stabilizer). The results of Krongauz et al. [27] showed a similar profile for PVC degradation (at 350 nm during 400 h under high temperature). In their results, HCl liberation starts at approximately 60 h after light exposure for PVC1 and at 145 h for PVC3, both presenting an autocatalytic profile after this period. Low initial HCl formation was observed by Krongauz et al. [27], which later increased (after 100 h) up to a point at which stabilization between the coefficients of the second reaction, i.e. \(k_2\) and \(k_i\), occurs [28].

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC1 and PVC3</td>
<td>(Y \text{ (kJ mol}^{-1})</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>(R \text{ (kJ mol}^{-1} \text{ K}^{-1})</td>
<td>8.314</td>
</tr>
<tr>
<td></td>
<td>(T \text{ (K)})</td>
<td>325</td>
</tr>
<tr>
<td></td>
<td>(\delta \text{ (cm)})</td>
<td>0.015</td>
</tr>
<tr>
<td></td>
<td>(\alpha \text{ (L mol}^{-1} \text{ cm}^{-1})</td>
<td>320</td>
</tr>
<tr>
<td></td>
<td>(I_0 \text{ (W m}^{-2})</td>
<td>550</td>
</tr>
<tr>
<td></td>
<td>(E_{\text{p}} \text{ (kJ mol}^{-1})</td>
<td>157.125</td>
</tr>
<tr>
<td></td>
<td>(k_2 \text{ (L mol}^{-1} \text{ s}^{-1})</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>(k_i \text{ (L mol}^{-1} \text{ s}^{-1})</td>
<td>160</td>
</tr>
<tr>
<td></td>
<td>(S \text{ (J)})</td>
<td>8,000</td>
</tr>
<tr>
<td></td>
<td>(n)</td>
<td>3</td>
</tr>
<tr>
<td>PVC1</td>
<td>(E_{\text{p}} \text{ (kJ mol}^{-1})</td>
<td>102.655</td>
</tr>
<tr>
<td></td>
<td>(k_2 \text{ (L mol}^{-1} \text{ s}^{-1})</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>(k_i \text{ (L mol}^{-1} \text{ s}^{-1})</td>
<td>160</td>
</tr>
<tr>
<td></td>
<td>(S \text{ (J)})</td>
<td>8,000</td>
</tr>
<tr>
<td></td>
<td>(n)</td>
<td>3</td>
</tr>
<tr>
<td>PVC3</td>
<td>(E_{\text{p}} \text{ (kJ mol}^{-1})</td>
<td>157.125</td>
</tr>
<tr>
<td></td>
<td>(k_2 \text{ (L mol}^{-1} \text{ s}^{-1})</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>(k_i \text{ (L mol}^{-1} \text{ s}^{-1})</td>
<td>160</td>
</tr>
<tr>
<td></td>
<td>(S \text{ (J)})</td>
<td>8,000</td>
</tr>
<tr>
<td></td>
<td>(n)</td>
<td>3</td>
</tr>
</tbody>
</table>

The simulation exercise depicted in Figs. 3–6 illustrates one of the possible applications of a PVC aging mathematical model to assess PVC performance without resorting to costly experimental procedures. However, a mathematical model demands experimental validation, at least for a few cases, so that the model results could be reliably extrapolated to similar configurations. The experimental validation of the mathematical model proposed was carried out based on available published experimental data for PVC1 and PVC3 samples [21,26].

For the experimental data [21,26] shown in Figs. 7 and 8, there was an initial whiteness of the samples, resulting from the photo-oxidation of the conjugated double bonds.
formed during processing of the filled polymer. The initial radical produced in the reaction shown in Fig. 1 is extremely unstable, and a series of electron-transfer reactions promote the elimination of free Cl\(^-\) and CO\(^2\). Because of this, an initial energy accumulation occurs, affecting the photochemical process and leading to colour changes [26,28,29]. The degradation process starts accelerating when the absorbed energy is sufficient to break double bonds and, after this, the chemical energy remains constant [28]. Real and Gardette [21] also showed the increase in absorption resulting from photo-oxidation of the conjugated double bonds formed during processing of the activated polymer. Jakubowicz [28] reported colour change differences under artificial weathering at 35 °C, which also qualitatively agrees with the numerical results obtained in this work.

The experimental validation of the numerical results is carried out in terms of PVC yellowing percent \(\Delta Y^0\), as shown in Figs. 7 and 8. The experimental data [21,26] shows an initial whitening effect which is not captured by the model. The reason is that the experiments directly measured absorbance, not [HCl], and compared it with absorbance standards of non-exposed PVC. Since absorbance decreases when the additives are exposed to light, the absorbance readings show negative values. On the other hand, in the model introduced in this paper, the values calculated with Eq. (9) cannot be negative, therefore the initial “whitening” effect cannot be captured, which is undoubtedly a limitation of the current model, but only in the initial degradation region. This could be solved in a future model improvement. Nevertheless, as the simulation proceeds in time, the numerical results start showing good quantitative and qualitative agreement with the experimental data for both samples, PVC1 and PVC3 (see Figs. 7 and 8, respectively).

Shi et al. [30] investigated the photodegradation of PVC samples with distinct degree of polymerization with respect to viscosity and molecular weight difference. Their results corroborate the findings of this work, since they also show sigmoid-shaped curves for all types of PVC.

5. Conclusions

In this paper, a simplified mathematical model to predict degradation of transparent poly(vinyl chloride) (PVC) in photobioreactors under a particular condition of light incidence was introduced. The model incorporates the concept of cooperative reactions and uses the Hill equation to model the behaviour of the reaction rate of PVC degradation, \(k_1\). The currently available models are frequently based on thermal degradation, especially under high temperatures. However, under the usual natural conditions of exposure, such models will not be fully capable of predicting polymer lifetime.

Previously published experimental data were used to validate the numerical simulation results obtained with the model, with good quantitative and qualitative agreement. A simulation exercise was conducted to demonstrate a possible scenario for assessment of PVC performance and lifetime with results reliability granted by the experimental validation procedure. The main conclusion is that PVC aging (or degradation) is well correlated by sigmoidal profiles allowing for realistic polymer lifetime predictions. As a result, the model is expected to be a useful tool for simulation, design and investigation of properties, and also for parameter optimization of PVC for minimum photodegradation.

Acknowledgements

The authors acknowledge with gratitude the support of the Brazilian National Council of Scientific and Technological Development, CNPq.

References


