



Anaerobic Biodegradability Modelisation of Cellulose Auto-Catalytic Model

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In this study, we described the biodegradation process of cellulose based on the Boltzmann distribution derived from autocatalytic kinetics. From the autocatalytic model (MAC) we concluded that the molecular weight, temperature, and the interaction parameter (x) (type of polymer and biodegrading agent) are the major factors governing the phenomenon of biodegradation. The modeled results and the experimental results, according to the ASTM D5511 protocol, present a good correlation.

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Introduction

Biodegradation is defined, according to US Environmental Protection Agency (EPA), 2009, as "the process by which microbial organisms transform or alter (through metabolic action, or enzymatic) the chemical structure introduced into an environment". While the biodegradability, according to EPA, is "the relative susceptibility to degradation resulting from the metabolism organic. The biodegradability is variable and depends on the type of product (polymer). In general, the biodegradability increases with the increase of the solubility, which is inversely proportional to molecular weight M_w ".

Enzymatic biodegradability [1, 2] and microbial [3-5] is a measurable parameter in the evaluation of the amount of CO_2 generated, the amount of O_2 consumed (aerobic), the variation of the molecular weight, the mass loss or other physical properties [6-9]. The biodegradability of the polymers in

general (especially cellulose) is not only conditioned by chemical factors (concentration, structure, etc.), but it is also highly dependent on the environmental factors such as weather conditions, the moisture, oxygen, organic matter, microorganisms, etc. The diversity and the large number of parameters governing the biodegradability limit the understanding of the kinetics and mechanisms. The modeling is a useful method and widely exploited for understanding the chemical processes in often complex degradation systems [10]. In this paper, we propose the Boltzmann distribution equation derived from the autocatalytic kinetic model to understand the change in the anaerobic biodegradability process of the cellulose material.

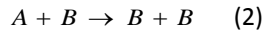
We assume in this study that all types of energy involved in the process of biodegradation ($\sum energy_{biod}$) are equivalent to thermal energy ($energy_{thermal}$):

$$\sum energy_{biodeg} = \sum energy_{thermal} \quad (1)$$

Development of autocatalytic model

Autocatalytic kinetics equation:

In general, the autocatalytic reaction between two reactants A and B can be schematized by the equation 2:



The rate law for this reaction is given by the equation (3):

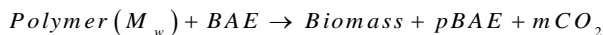
$$\frac{-d[A]}{dt} = K[A][B] \quad (3)$$

$$[B]_t = \frac{[A]_0 + [B]_0}{1 + \frac{[A]_0}{[B]_0} \exp\left(\left([A]_0 + [B]_0\right)kt\right)} \quad (4)$$

Over time and under the action of the biodegradation agents, the rate of the biodegradation reaction starts substantially low in the early stages and increases to reach the maximum and then decreases and becomes zero. In contrast, in the case of the "Ekenstam" kinetic, the rate begins at maximum value then decreases towards zero.

In addition, the kinetic of a reaction, by definition, is the variation of such physical property describing the state of the reaction system as a function of time, and we have chosen for this study the molecular weight as a determinant parameter of biodegradation study.

We can consider the process of biodegradation as an autocatalytic reaction schematized by the reaction equation below:



Where:

Polymer (M_w): the polymer having a molecular weight M_w

BAE: bioactive element.

p: the stoichiometric coefficient of the BAE at the end of the biodegradation reaction.

m: the stoichiometric coefficient of the carbon dioxide resulting from the biodegradation.

We propose in this study the molecular weight as the physical property describing the state of the biodegradation system over time. According to the autocatalytic kinetic law (equation 4), the kinetic equation that describes the variation of the molecular weight of the polymer has the following solution:

We deduce then, the expression of the interaction term x as follows:

$$M_w(t) = \frac{M_w(0) + \mu_{BAE}}{1 + \frac{M_w(0)}{\mu_{BAE}} \exp\left(t(M_w(0) + \mu_{BAE})k_{bd}\right)}$$

$$= (M_w(0) + \mu_{BAE}) - \frac{M_w(0) + \mu_{BAE}}{1 + \frac{M_w(0)}{\mu_{BAE}} \exp\left(-t(M_w(0) + \mu_{BAE})k_{bd}\right)} \quad (5)$$

μ_{BAE} is a constant that depends on the BAE-polymer interactions (the average molecular weight of BAE interaction at $t = 0$) and k_{bd} is the rate constant of the biodegradation reaction.

Assuming that:

$$\mu_{BAE} = xM_w(0) \quad (6)$$

The $M_w(t)$ take then the form showed in the equation (7).

$$M_w(t) = M_w(0)(1+x) - \frac{M_w(0)(1+x)}{1 + \frac{1}{x} \exp\left(-t(M_w(0)(1+x))k_{bd}\right)} \quad (7)$$

We normalize the molecular weight and we get the following expression:

$$\frac{M_w(t)}{M_w(0)} = \alpha(t) = (1+x) \left\{ 1 - \frac{1}{1 + \exp\left(\frac{t - \frac{\ln \frac{1}{x}}{(M_w(0)(1+x))k_{bd}}}{\frac{1}{(M_w(0)(1+x))k_{bd}}}\right)} \right\} \quad (8)$$

The second derivative of equation (8) is zero at t_{Vmax} where t_{Vmax} is the time required to reach the maximum rate of the biodegradation and has the following expression:

$$t_{Vmax} = \frac{\ln \frac{1}{x}}{(M_w(0)(1+x))k_{bd}} \quad (9)$$

The time to reach the maximum speed of biodegradation (t_{Vmax}) depends on the initial molecular weight of the polymer, the type of the bioactive element and the temperature.

Whether

$$dt = \frac{1}{(M_w(0)(1+x))k_{bd}} \quad (10)$$

$$x = \exp\left(-\frac{t_{v\max}}{dt}\right) \quad (11)$$

We get:

$$\alpha(t) = \frac{1+x}{1+\exp\left(\frac{t-t_{v\max}}{dt}\right)} \quad (12)$$

Equation (12) is a Boltzmann distribution, which describes the autocatalytic kinetics and it, can be written in the form below:

$$\alpha(t) = \frac{A-B}{1+\exp\left(\frac{t-t_{v\max}}{dt}\right)} + B \quad (13)$$

Where:

B is the fraction of non biodegraded molecular weight, which is not converted into carbon dioxide and methane throughout time λ , dt is the Boltzmann slope factor. A and B, in other words, are the ends of the normalized weight distribution curve where $d\alpha(t)/dt = 0$:

$$A = 1+x \text{ and } B = \alpha(t=\lambda)$$

The equation (13) becomes:

$$\alpha(t) = \frac{(1+x) - \alpha(t=\lambda)}{1+\exp\left(\frac{t-t_{v\max}}{dt}\right)} + \alpha(t=\lambda) \quad (14)$$

The rate of biodegradation, then, is given by the value of $(1-\alpha)$.

The rate constant of biodegradation K_{bd}

The activation energy E_a is, by definition, the energy barrier to trigger a reaction. Assuming in the case of a biodegradation reaction, the bioenergetics barrier is equivalent to the thermal barrier degradation. Indeed, considering the energy value and not its appearance and its nature, the thermal effect on the degradation of the polymer can be assimilated to the action of bioactive components (bacteria, fungi, etc.).

The biodegradation rate constant (k_{bd}) can be estimated using the results of thermo gravimetric analysis (TGA), from the Arrhenius law [11]:

$$k_{bd} = A_0 \sqrt{T} \cdot \exp\left(-\frac{E_a}{RT}\right) \quad (15)$$

Activation energy E_a and the pre-exponential factor $A_0(T)^{1/2}$ can be estimated from the thermogravimetric analyzes.

The determination of kinetic parameters was the subject of many research areas; the dynamic method is one of the methods that have attracted the attention of experimenters. It consists in tracing the natural logarithm of the heating rate ($\ln\beta$) as a function of the inverse of the temperature at the maximum degradation (T_{max}) [12]:

$$\ln \beta = \ln A_0 + \frac{3}{2} \ln T_{max} - \ln\left(\frac{E_a}{RT_{max}} + \frac{1}{2}\right) - \frac{E_a}{RT_{max}} \quad (16)$$

From equation (16) the variation of the heating rate logarithm is inversely proportional to the maximum temperature of thermal degradation (T_{max}). The curve is a line with slope $(-E_a/R)$. To determine A_0 , then just replace the values of E_a , β and T_{max} in equation (16).

Model verification

Determination k_{bd}

Cellulose 20 μ m with molecular weight ~ 36300 [13] has been selected as sample application to justify the model described. The results of the thermal analysis (TGA) of the cellulose used (Fig 1) are extracted from the thesis work of Cedric Reverte, 2007 [14].

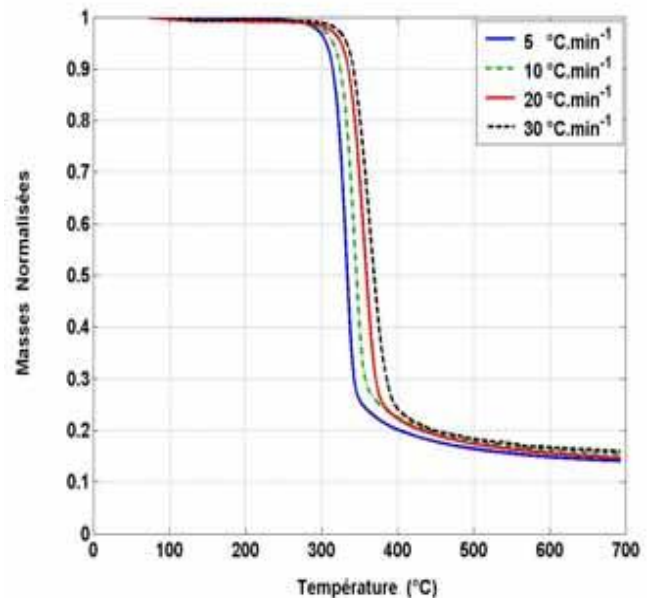


Fig. 1: Experimental mass "raw" standard, according to the temperature in ° C of the thermal degradation of cellulose, for heating rates equal to 5, 10, 20 and 30 ° C.min

By the method of tangents we determine the temperature of the maximum degradation rate, then we trace the curve $\ln\beta = f(1/T_{max})$ to determine the activation energy (Fig 2):

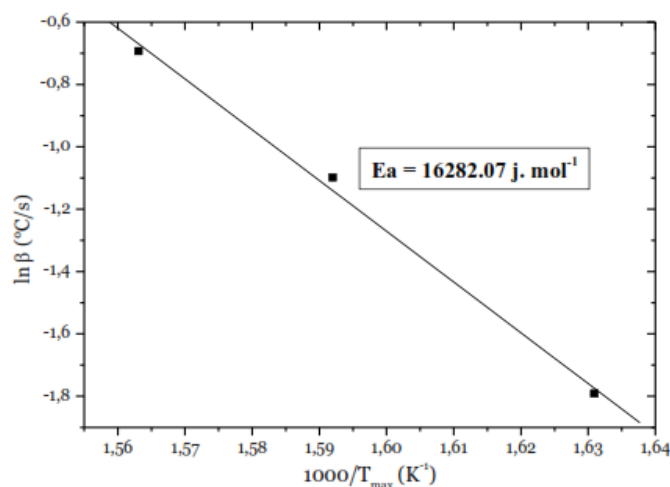


Fig. 2: The curve $\ln \beta = f(1/T_{\max})$ to determine the activation energy

Substituting the value of the activation energy in equation (18) at 52°C, and the value of the constant biodegradation was obtained:

$$k_{bd} = 2.73 \cdot 10^{-07} \text{ h}^{-1}$$

Cellulose biodegradation prediction

The experimental results are performed by NSF International Standard using ASTM D5511 at 52 °C [15] and compared to modeled results (fig 3):

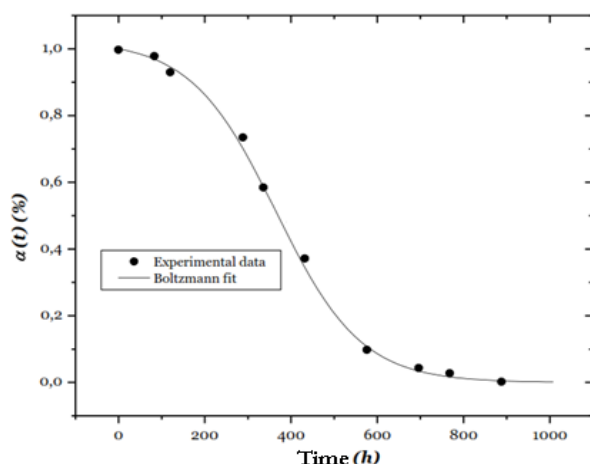


Fig. 3: Experimental results and regressed to the normalized variation of molecular weight during the anaerobic biodegradation ASTM D5511.

The analysis of these results and their Boltzmann regression lead to the new equation:

$$\alpha(t) = \frac{1 + 0.0246}{1 + \exp\left(\frac{t - 357.75}{114.82}\right)} \quad (17)$$

From the Boltzmann regression we determined the bio-interaction parameter $x \sim 0.0246$ and $A \sim 1.0246$, since the degradation is complete, so ($B = 0$). We replace in equations 9 and 10:

$$t_{v \max} = \frac{\ln \frac{1}{x}}{M_w(0)(1+x)k_{bd}} = 365 \text{ h}$$

$$dt = \frac{1}{M_w(0)(1+x)k_{bd}} = 98.5 \text{ h}$$

Conclusion

This study was performed to model the phenomenon of the anaerobic biodegradation of cellulose. From the experimental results according to the ASTM D5511 protocol, we described the biodegradation process based on the model Boltzmann derived from autocatalytic kinetics. Moreover, from the autocatalytic model (MAC) we concluded that the molecular weight, temperature, and the interaction parameter (x) (type of polymer and biodegrading agent) are the major factors governing the phenomenon of biodegradation.

Also, we suggest that the interaction parameter (x), setting the experimental conditions, depends on the chemical structure of the polymer studied, and therefore, this parameter will be linked to the solubility parameter.

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