

Mathematical Model of Water Absorption in Arrowroot Starch-Chitosan Based Bioplastic

by Yusmardhany Yusuf

Submission date: 20-May-2022 06:06AM (UTC+0700)

Submission ID: 1840160491

File name: 6310-18650-2-PB.pdf (452.05K)

Word count: 2516

Character count: 12504

Mathematical Model of Water Absorption in Arrowroot Starch-Chitosan Based Bioplastic

Yusmardhany Yusuf^{*}, Fauzan Irfandy, dan Alit Istiani

Program Studi Teknik Kimia, Jurusan Teknik Kimia, Fakultas Teknik Industri, Universitas Pembangunan Nasional "Veteran" Yogyakarta,
Jl. SWK 104 (Lingkar Utara) Condongcatur, Yogyakarta, 55283, Indonesia

Artikel histori :

Diterima 4 Desember 2021
Diterima dalam revisi 2 Maret 2022
Diterima 23 Maret 2022
Online 5 April 2022

ABSTRACT: Expansion of the size of the weight of bioplastics often occurs in daily use. This phenomenon happens because the material from bioplastics can absorb significant amounts of water. This process can lead to accumulation of swelling degree. Therefore, a mathematical model is needed to quantify this mechanism to predict the dynamics of changes in the weight of bioplastics with respect to time while contact with water to help practitioners during application design for the use of bioplastics. This study aims to build a mathematical model derived from the mass sense validated by experimental data through curve fitting. The experiment was conducted by observing the rate of change in the mass of bioplastic made from starch and chitosan by measuring the change in mass concerning time immersed in water under atmospheric conditions. The immersion time was varied between 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 20, 30, 40, 50, and 60 minutes. As a result, it can be concluded that starch-chitosan-based biofilms can absorb water up to ± 10.9174 gr-water/gr-bioplastic, and also this phenomenon can be quantified by a mathematical equation that derived from mass balance with an average percent error of 1.13% and R-squared coefficient of 0.9981.

Keywords: Bioplastics, chitosan, starch, swelling, biofilms

1. Introduction

Based on data, it is estimated that in 2025 there will be 7.42 million tons of plastic waste that is not handled (Jambeck et al., 2015; Ritchie and Roser., 2018). Consequently, it can threaten the environment and health due to hazardous toxic materials such as phthalates, poly-fluorinated chemicals, bisphenol A (BPA), brominated flame retardants, and antimony trioxide (Alabi et al., 2019). Consequently, environmentally friendly materials are needed to replace plastic from petroleum materials.

One such alternative is a bioplastic made from starch, composed of protein, pectin, gum, starch, and fat. Unfortunately, the essential ingredient of starch has a weakness: the number of hydroxyl groups that contribute to the solubility value in water (Koo, Lee, and Lee., 2010; Woggum and Wittaya., 2015; Shah, Mewada, and Mehta., 2016). This mechanism can lead to accumulation of swelling degree. Therefore, starch modification is significant to overcome these weaknesses by employing several modifications such as chemical, physical, and enzymatic methods. Among these methods, cross-linking is the most commonly used chemical method, this method has the advantages

of resistance to heat, mechanical stress, and resistance to acid (Munawaroh., 2015).

Several previous works for mathematical models on starch-chitosan had been reported: Malumba et al. (2013) fitted third-order kinetic and Weibull empirical equation to understand the time-temperatures dependence of swelling behavior of wheat starch granule. Bourtoom and Chinnan (2015) observed an increase in tensile strength, water vapor permeability, lighter color and yellowness, a decreasing elongation at the break, and film solubility. Desam et al. (2019) proposed a pseudo-first- and second-order kinetic and Weibull model for swelling kinetics of rice and potato starch suspensions during the investigation, granules were subjected to heating at 60, 65, 70, 75, 80, and 85 °C within 0-60 minutes holding times.

Based on the previous works above, we do not find a study of swelling rate phenomena from arrowroot starch-chitosan. However, since arrowroot is abundant in Indonesia is necessary to investigate arrowroot starch-chitosan absorption to prepare good quality bioplastic production.

In this study, we aimed to build the mathematical model for the accumulation of water absorption by observing the change of mass in arrowroot starch-

^{*}Corresponding Author
Email: yusmardhany.yusuf@upnyk.ac.id

chitosan based bioplastic in the following immersion time interval: 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 20, 30, 40, 50, and 60 minutes under room temperature and pressure. The mathematical model was derived from mass balance under unsteady-state conditions, governed by convective mass transfer.

2. Materials and Methods

2.1. Material

Starch was collected from Arrowroot (*Maranta Arundinacea L*). This plant was used as a biodegradable film construction material. Chitosan addition materials, crosslinkers in acetic acid, and plasticizers in the form of glycerol are used for biodegradable film modification.

2.2. Preparing and Casting

The starch, glycerol, and chitosan were weighed with each weight ratio of 3:1:1, and poured into 100 mL of beaker glass, and then added by 50 ml of distilled water. The solution was mixed using a magnetic stirrer at a temperature of 70°C within 5 minutes. After that, The casting was prepared by pouring the mixture into a petri dish, then it was put in the oven by setting the temperature at 40 °C followed by peeling the dried film from the cup.

2.3. Method of Analysis

The biofilm samples were cut to a size of 2 cm x 2 cm and then immersed in distilled water at the following time intervals: 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 20, 30, 40, 50, and 60 minutes. Then the soaked samples were weighed according to the time intervals specified above. The swelling rate was carried out by varying the immersion time above. The data were collected twice. After that, the data were averaged.

2.4. Mathematical Derivation

We assume that the swelling degree process begins from by following mechanisms:

1. Water is absorbed into biofilm materials due to the driving force mechanism within differential concentrations of water at interphase (c_w^*) and biofilm body over time (c_w), respectively. These phenomena are expressed mathematically by:

$$\Delta c = (c_w^* - c_w) \quad (1)$$

c_w was given from net of mass within bioplastic (m_B) and initial mass of bioplastic (m_B^0) divided by m_B^0 as described below:

$$c_w = \frac{m_B - m_B^0}{m_B^0} \quad (2)$$

2. Since water absorption happens within the interphase and solid phase, the mass transfer rate is also governed by the convective mass transfer coefficient (k_c). Then the rate of input can be expressed by:

$$m_{in} = k_c \Delta c V_B \quad (2)$$

$$\dot{m}_{in} = k_c (c_w^* - c_w) V_B \quad (3)$$

Where V_B = Volume of bioplastic

3. Equation 3 is called the rate of input of water, and since there is neither water leaving nor generated, then the accumulation of water to time (t) within a biofilm can be expressed by:

$$V_B \frac{dc_B}{dt} = k_c (c_w^* - c_w) V_B \quad (4)$$

Since V_B is constant, then:

$$\frac{dc_B}{dt} = k_c (c_w^* - c_w) \quad (5)$$

4. To solve m_w we must integrate equation (5) by the general solution we have:

$$c_w = c_w^* + C_1 e^{-k_c t} \quad (6)$$

To satisfy the initial condition $c_w(0) = 0$, C_1 constant should be:

$$C_1 = -c_w^* \quad (7)$$

Then the equation (5) turns into

$$c_w = c_w^* (1 - e^{-k_c t}) \quad (8)$$

Finding Variables

There are two unknown variables c_w^* and k_c . Since the equation is nonlinear, these variables are solved iteratively by the newton method for a system of nonlinear equations (Hermawan & Kholisoh, 2021) in SCILAB software. The flowchart can be seen in **Figure-1**.

After giving an initial condition for variables c_w^* and k_c we need to declare $f(t)$, $\frac{\partial f(t)}{\partial c_w^*}$ and $\frac{\partial f(t)}{\partial k_c}$.

Let re-arrange equation (7) into:

$$f(t) = c_w - c_w^* (1 - e^{-k_c t}) \quad (8)$$

Then for the derivative function, we have:

$$\frac{\partial f(t)}{\partial c_w^*} = -(1 - e^{-k_c t}) \quad (9)$$

$$\frac{\partial f(t)}{\partial k_c} = -c_w^* t e^{-k_c t} \quad (10)$$

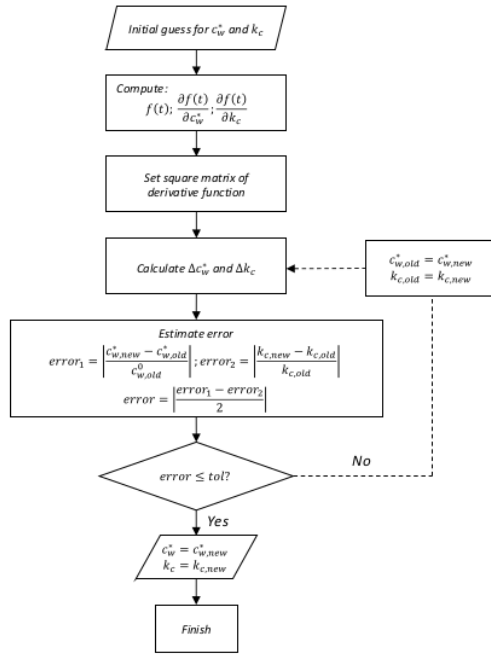


Figure-1. Flowchart of Nonlinear Newton Method

The set of a square matrix will be in the form:

$$\begin{bmatrix} \frac{\partial f(t_1)}{\partial c_w^*} & \frac{\partial f(t_1)}{\partial k_c} \\ \frac{\partial f(t_2)}{\partial c_w^*} & \frac{\partial f(t_2)}{\partial k_c} \\ \vdots & \vdots \\ \frac{\partial f(t_n)}{\partial c_w^*} & \frac{\partial f(t_n)}{\partial k_c} \end{bmatrix} \begin{bmatrix} \Delta c_w^* \\ \Delta k_c \end{bmatrix} = \begin{bmatrix} f(t_1) \\ f(t_2) \\ \vdots \\ f(t_n) \end{bmatrix} \quad (11)$$

Also, the tolerance is set to 1×10^{-6} to satisfy the error value.

Presenting Error

We present the error within observed and estimated of m_w in two methods to validate the model: deviation data and correlation coefficient of R.

The formula for individual error:

$$error(t) = \left| \frac{c_{w,data}(t) - c_{w,estimated}(t)}{c_{w,data}(t)} \right| \times 100\% \quad (12)$$

Average error:

$$\overline{error} = \frac{\sum_i^n error(t)}{n} \quad (13)$$

The formula for correlation coefficient of R:

$$r = \frac{n(\sum xy) - (\sum x)(\sum y)}{\sqrt{[n\sum x^2 - (\sum x)^2][n\sum y^2 - (\sum y)^2]}} \quad (14)$$

where:

$$x = m_{w,data}$$

$$y = m_{w,estimated}$$

This equation will tell us how strong the linear relationship within observed and estimated data of m_w . As the coefficient of R^2 is closer to 1, the more represented the estimated data to the actual data.

3. Result and Discussion

3.1. Estimation of absorbed water in bioplastic

Table-1 and Figure-2 show the mass changes at each time point within sixteen data points, respectively. As can be seen, the mass of bioplastics accelerated rapidly to a maximum of 0.1850 grams at the 40th minute. Above 40th-minute bioplastic, the mass has tended to constant strictly at 50th and 60th minutes. Due to the large amount of water absorbed by bioplastic, the water content in the bioplastic goes saturated.

We fitted Equation-7 based on data mass of water in bioplastic versus time. Since the inflection point began to form above the 10th minute, we use 0.16 and 1/10 as an initial guess for m_w^* and k_c , respectively.

As described in the Equation-2 mass of bioplastic is calculated based on the total bioplastic mass over time. These data will be used as a reference for a curve in fitting, as described in Equation-7.

Table-1. Mass of bioplastics and water over time

No	t (mins)	m_B (gram)	c_w ($\frac{g_water}{g_bioplastic}$)
1	0	0.0152	0.0000
2	1	0.0819	4.3882
3	2	0.1230	7.0921
4	3	0.1457	8.5855
5	4	0.1562	9.2763
6	5	0.1654	9.8816
7	6	0.1729	10.3750
8	7	0.1758	10.5658
9	8	0.1765	10.6118
10	9	0.1793	10.7961
11	10	0.1823	10.9934
12	20	0.1828	11.0263
13	30	0.1829	11.0329
14	40	0.1850	11.1711
15	50	0.1788	10.7632
16	60	0.1788	10.7632

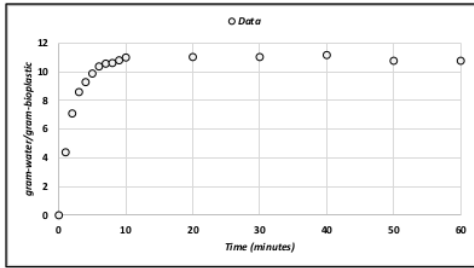


Figure-2. The evolution of the mass of bioplastics in water over time

3.2. Estimating the constant value by curve fitting calculation

From curve fitting, we got constant values 10.9174 and 0.5053 for c_w^* and k_c , respectively. This constant means that the maximum absorbed water is 10.9174 gr-water/gr-bioplastic, and the convective mass transfer coefficient of absorbed water is 0.5053/minute.

As validation within observed data and estimated, we compute error and R-squared value 1.13% and 0.9981, respectively. These two data indicate that the equation can show the phenomena of absorbed water in bioplastic. Final tabulation observed data and estimated are presented in Table-2, Figure-3, and Figure-4.

Table-2. Comparison observed data vs. estimated and error percentage

No	t (mins)	c_w (Data)	c_w (Estimated)	Error
1	0	0.0000	0.0000	0.0000
2	1	4.3882	4.3304	1.3162
3	2	7.0921	6.9431	2.1004
4	3	8.5855	8.5195	0.7686
5	4	9.2763	9.4707	2.0950
6	5	9.8816	10.0455	1.6488
7	6	10.3750	10.3907	0.1517
8	7	10.5658	10.5996	0.3204
9	8	10.6118	10.7257	1.0728
10	9	10.7961	10.8017	0.0526
11	10	10.9934	10.8476	1.3264
12	20	11.0263	10.9170	0.9918
13	30	11.0329	10.9174	1.0468
14	40	11.1711	10.9174	2.2706
15	50	10.7632	10.9174	1.4331
16	60	10.7632	10.9174	1.4331
<i>Average=</i>			1.1268	

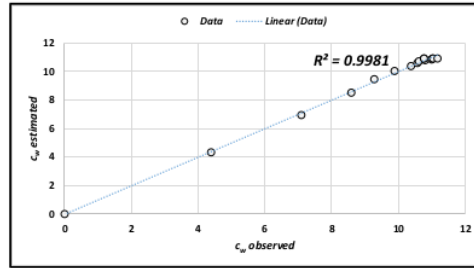


Figure-3. Cross plot of c_w observed and estimated

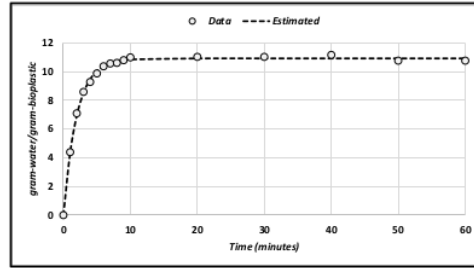


Figure-4. Curve fitting based on the developed mathematical model

4. Conclusions

The conclusions obtained from this study are as follows:

1. The mass of water concentration in bioplastic is estimated to be $10.9174 \frac{\text{gr-water}}{\text{gr-bioplastic}}$ after 30 minutes of immersion in water for the given sample size of 2 cm x 2 cm.
2. The absorption phenomena can be represented by an equation, as follow: $c_w = c_w^* + C_1 e^{-k_c t}$

Where:

$$c_w^* = 10.9174 \frac{\text{gr-water}}{\text{gr-bioplastic}}$$

$$k_c = 0.5053/s$$

Acknowledgment

This research is funded by Lembaga Penelitian dan Pengabdian Masyarakat (LPPM) Universitas Pembangunan Nasional "Veteran" Yogyakarta.

References

- Jambeck, J.R., Geyer, R., Wilcox, C., Siegler, T. R., Perryman, M., Andrady, A., Narayan, R., & Law, K. L., 2015, Plastic waste inputs from land into the ocean. *Science Vol. 347 No. 6223*, Februari: 768-771
- Ritchie, H., and M. Roser, 2018, Plastic pollution, <https://ourworldindata.org/plastic-pollution> (19 Juli 2021)
- Alabi, O.A., Ologbonjaye, K.I., Awosolu, O., & Alalade, O.E., 2019, Public and environmental health effects of plastic wastes disposal: a

- review. *Journal of Toxicology and Risk Assessment Vol. 5 No. 21*, April:1-13
- Koo, S.H., Lee, K. Y. & Lee, H. G., 2010, Effect of cross-linking on the physicochemical and physiological properties of corn starch. *Food Hydrocolloids Vol.24 No.6-7*, August: 619-625.
- Wogugum, T., Sirivongpaisal, P., & Wittaya, T., 2015, Characteristics and properties of hydroxypropylated rice starch based biodegradable films. *Food Hydrocolloids Vol.50*, Agustus: 54-64.
- Shah, N., Mewada, R. K., & Mehta, T., 2016, Crosslinking of starch and its effect on viscosity behaviour. *Review in Chemical Engineering Vol.25 No.2*, Januari: 265-270.
- Munawaroh, A., 2015, Pemanfaatan Tepung Kulit Pisang (*Musa paradisiaca*) dengan Variasi Penambahan Gliserol Sebagai Bahan Alternatif Pembuatan Bioplastik Ramah Lingkungan. *Doctoral dissertation of Faculty of Teacher Training and Education*, Indonesia: Universitas Muhammadiyah Surakarta.
- Malumba, P., Jacquet, N., Delimme, G., Lefebvre, F., & Béra, F., 2013, The swelling behaviour of wheat starch granules during isothermal and non-isothermal treatments. *Journal of Food Engineering Vol.114 No.2*, Januari: 199-206.
- Bourtoom, T., & Chinnan, M. S., 2008, Preparation and properties of rice starch-chitosan blend biodegradable film. *LWT-Food science and Technology Vol.41 No.9*, November: 1633-1641.
- Desam, G.P., Li, J., Chen, G., Campanella, O., & Narsimhan, G., 2020, Swelling kinetics of rice and potato starch suspensions. *Journal of Food Process Engineering Vol.43 No.4*, Desember: e13353.
- Hermawan, Y.D. & Kholisoh, S.D., 2021, *Metode newton untuk persamaan Tak-Linier*. Modul Praktikum Analisis Numerik dan Pemograman dengan Scilab. hlm. IV-5. Yogyakarta: Laboratorium Komputasi Proses Jurusan Teknik Kimia-Fakultas Teknik Industri UPN "Veteran" Yogyakarta

Mathematical Model of Water Absorption in Arrowroot Starch-Chitosan Based Bioplastic

ORIGINALITY REPORT

4%

SIMILARITY INDEX

6%

INTERNET SOURCES

5%

PUBLICATIONS

6%

STUDENT PAPERS

MATCH ALL SOURCES (ONLY SELECTED SOURCE PRINTED)

3%

★ jurnal.upnyk.ac.id

Internet Source

Exclude quotes Off

Exclude matches < 2%

Exclude bibliography Off