

Sorption characteristic of organic liquid and its effect on the mechanical performance of a PLA-based plastic

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ABSTRACT: The objective of this article is to assess the mechanical performance of PLA-based materials under exposure of an organic liquid. In evaluating new opportunities of PLA-based material, it is important to understand not only the chemical resistance of the material but also the potential route for degradation, which affect the mechanical behavior of the product during its service time. Degradation of PLA material with amount of sorption should be carefully controlled in order to maintain its mechanical performance in response to various loading condition. Distribution of the absorbed liquid within the package is firstly evaluated by identifying the characteristics of the mass transport. Gravimetric analysis is employed to investigate the liquid sorption mechanism and the induced expansion over a particular period. The profile of absorbed liquid content is numerically obtained and verified with the analytic solution. The changes in mechanical performances were investigated by measuring the properties of specimens containing saturated liquid content. It is found that at low temperature, the kinetics of liquid sorption follows the Fick's law but at higher temperature, it showed a deviation from the Fickian curve. The experiment results also confirm progressive decrease of the modulus and strength by increasing of fluid content inside the material. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43250.

KEYWORDS: biodegradable; degradation; mechanical properties

Received 12 August 2015; accepted 23 November 2015

DOI: 10.1002/app.43250

INTRODUCTION

Poly lactide acid (PLA) is an aliphatic polyester derived from renewable resources, which has been receiving attention to be used as a commodity thermoplastic in several applications. Despite possessing good mechanical and optical properties, deterioration of the material properties in PLA-based materials could occur after prolonged exposure to the environment during their service time. Diffusion of external molecules from the environment can change the properties of material which alter the capability of the product as required.

Dependence of material properties on absorbed substances is of concern especially in the relatively thick product design since time taken to reach saturated concentration is proportional to the thickness. In many applications, the mass transport is likely to be a transient rather than steady state. The diffusion of a liquid substance, for example, may take quite long period of time for reaching a saturated condition. Because of time and spatial variation of absorbed substance, in-homogeneous properties may occur within the material. Therefore, an understanding of mass transport characteristics is essential to specify accurate

material properties data used in analyzing mechanical behavior of the material. The material properties depend on the composition (coating, blending, filler), but the behavior of material in contact with the environment may affect durability of the material during its service lifetime.

Numerous researches have observed the effect of environment condition on PLA materials.^{1–5} The decreasing of mechanical performance has been reported after absorbing moisture under particular humidity condition. As the majority of existing commercial applications are for food packaging, the studies on the sorption of product constituent by the PLA material mainly focused on the barrier properties of food solutions related to the quality of the packaged product.^{6–9} Recent reports on interaction between PLA package and its product constituent revealed changes of thermomechanical properties after sorption of a hydrophilic chemical compound into the package.^{7,10,11} This finding signified sorption-induced plasticization in PLA package during its interaction with a particular substance of a packaged product.

The mass transport in PLA materials in forms of gas and liquid has been deeply examined by some researchers.^{3,4,6,12} Some

disagreements in sorption mechanism of moisture have been found in the literature. One study observed a typical Fickian diffusion which is a rapid uptake in the first period followed by a slower approach toward constant moisture content indicating equilibrium.⁴ Another study shows similar behavior in the initial phase, however equilibrium conditions cannot be attained after quite long period of exposure time.³ In the case of aroma compound sorption, Auras⁶ showed a typical Fickian characteristic in PLA specimens with $23.2 \pm 1.78 \mu\text{m}$ thickness which took more than 30 days to have a saturated weight gain at 30 °C. Particularly relevant in applications for plastic water bottles and coated drug eluting stents, some investigations have focused on sorption and diffusion of liquid water in PLA.^{13,14}

Growing awareness in eco-friendly material has led to rising demand for application of PLA-based material in broader array of products. More semi-durable and rigid PLA packaging has been brought to and widely accepted into market, not only for food related products but also for consumer products. Finding new applications of PLA package for non-food commodities and other products is a logical consequence of an increasing environmental awareness. In evaluating new opportunities of PLA-based material for application exposed to chemical product or other aggressive liquid, it is important to understand not only the chemical resistance of the material but also the potential route for degradation.¹⁵ The diffusion of chemicals within plastic materials may also affect the mechanical performance of material. Information regarding the chemical mass transport through a plastic package is essential for understanding the accumulation of chemical inside the package and providing prediction of performance degradation. Degradation of PLA material with amount of sorption should be carefully controlled in order to avoid the structure deteriorating before end of its useful lifetime. With the expectation to use PLA-based material as an alternative material for application in contact with chemical or other organic liquid, a critical evaluation of material degradation is needed to predict the reliability and failure behavior of such applications. These are important areas in the development of models for predicting the mechanical behavior of a bio-based packaging in which the performances decrease with degradation.

This article presents the study of an organic liquid sorption in PLA material using simple gravimetric method following experimental work on immersion. Gravimetric sorption methods which measure change of mass are commonly used in investigating liquid sorption in polymeric materials.¹⁶ Actually, gasoline, a type of an organic liquid, is one of the most aggressive fluids to many commercial polymers. A study found that unleaded gasoline has greater effect on the performance of a polypropylene compared to water, chemical solutions (base and acid solvent), and diesel engine oil.¹⁷ The study is designed to model reasonable “worst” case extraction when the polymer is used in commercial fluid container application for intermediate time periods at various temperatures using the considerably aggressive fluid simulant. This model fluid was chosen in this study to test the performance of PLA in a rather unfavorable case. It is expected that the model fluid will be aggressive enough to accelerate the degradation in PLA material in a short

time. Changes of performance on the PLA-based material during diffusion of liquid which is represented by its mechanical properties will be investigated following the sorption study. The mechanical properties of material are necessary in evaluating stability of material during the entire service life of a component.

MATERIALS AND METHODS

Materials

The plastic material used in this study was a starch-based PLA resin produced by BIOTEC, a subsidiary company of Biome Technologies, which is known as Bioplast GS2189.¹⁸ This compound polymer is composed of 90% corn-derived PLA and reinforced with 10% potato starch.¹⁹ The material, which was supplied in granule form, was converted into test samples according to the manufacturer's product manual using a Battenfeld BA 350/75 injection moulding machine.

The immersion fluid for conducting this experiment is gasoline provided by a local fuel station, which constitutes of 50/50 toluene-iso octane mixture. In varying levels of fluid concentration, different immersion temperatures were used to accelerate the level of liquid absorption. Unleaded gasoline was chosen as aggressive enough to accelerate the degradation that would occur in an application exposed to liquid and chemical solvent.

Immersion Method

Standard test method of SAE J1748 was used in the immersion test. This method provides standard for determining physical property of polymer material exposed to gasoline/oxygenated fuel mixture. The rectangular injection-moulded samples in the size of ASTM D256 standard rectangular izod impact specimens ($63.5 \times 13 \times 3 \text{ mm}$) were completely immersed in hydrocarbon liquid in a ratio of three samples to 50 mL of liquid. Specimens were hanged with a stainless steel wire and separated with glass beads. The tubes were covered and the samples were immersed to the point of saturation under three different conditions: (1) room temperature where the temperature was monitored with a digital thermometer at $20 \pm 3 \text{ }^\circ\text{C}$, (2) a fridge with temperature monitored at $5 \pm 1 \text{ }^\circ\text{C}$, and (3) a thermal chamber set at 30 °C. Gravimetric measurement was used to determine the fluid uptake during the diffusion process. The specimens were removed periodically for weight measurement until the saturation occurs.

The apparent weight gain, ΔM is calculated using the following relationship:

$$M_t(\%) = \frac{m_t - m_0}{m_0} \times 100 \quad (1)$$

where m_0 and m_t are the weight of dry specimen before and during ageing, respectively.

Determination of equilibrium is based on standard recommended by SAE J1748, which compares data from two or more period to see no significant difference among the periods.²⁰ Once it has been determined that equilibrium has been reached, the equilibrium weight gain can be determined as an average from the last two consecutive weighting.

Testing on Mechanical Properties

In evaluating changes of mechanical properties with the amount of liquid absorption, mechanical tests are performed in saturated specimens to represent the properties in a particular liquid content. It is to ensure that mechanical properties are measured in specimens containing uniform liquid content²¹ thereby allowing more accurate relationship between the two parameters. Mechanical tests in nonimmersed (dry) samples are carried out to obtain results with zero liquid content in the same manner as with the immersed samples. Before measurement, the specimens are placed in another container at the standard laboratory temperature to effect cooling prior to testing. Testing is completed within 5 min of removal from the cooled fluid to minimize effect of dry out.

Tensile testing was performed under an international recognized standard, the ASTM methods D638: Standard test method for tensile properties of plastics. The “dog bone” shaped samples produced by injection moulding machine. Width and thickness of each sample required to calculate the area were measured using a Kincrome digital vernier caliper with resolution of 0.01 mm. The samples were tested to failure under tension at a cross head speed of 50 mm/min by using Zwick Z010 Universal Testing machine with a pre-load of 0 N.

Flexural tests were done using the same Zwick universal testing machine Z010 used for tensile testing with the 3-point bending rig setup. Testing procedure was performed following ASTM D790: Standard test method for flexural properties of unreinforced and reinforced plastics. The rectangular samples produced using injection moulding machine were used in this test. Testing was performed with 5 mm radius loading nose and 5 mm radius support with a pre-load of 0.2 N. The load was placed midway between the supports with a span of 40 mm. The crosshead speed applied was 1 mm/min. The TestXpert software version 8.1 was used to identify flexural strength of each sample tested.

The notched Izod impact strength test was conducted on a Resil 25 (CEAST) impact tester according to ASTM D256 at room temperature. Impact strength was measured as impact energy required per width of specimen. At least five specimens of each sample were tested to obtain the average value of the mechanical parameters and their standard deviation. The samples tested were rectangular samples made using the injection moulding machine and notched. The specimen is placed in the vise which is then submitted to the strike of the pendulum. The measured output from the instrument is the estimated breaking energy while simultaneously subtracting the compensation energy, which consist of the friction and wind age energy. The test may result in one of three types of failures in the specimen i.e., a complete break, a partial break (hinge), or a nonbreak.

RESULTS AND DISCUSSION

Experimental Result on Diffusion

Among several models describing the sorption phenomena in polymer, the Fick's diffusion model is the simplest and the most

widespread model satisfactorily applied in many polymeric materials with certain temperature ranges. The Fick's second law is defined as follows²²:

$$\frac{\partial C}{\partial t} = \nabla \cdot (D \nabla C) \quad (2)$$

where D is diffusion coefficient and C is diffusant concentration

In a case of infinite plate with thickness δ assuming that the concentration varies only in the z direction (one-dimensional), the diffusant concentration C as a function of position z and time t can be obtained as the solution of eq. (2) under specified boundary conditions as

$$C(z, t) = C_m \left(1 - \frac{4}{\pi} \sum_0^{\infty} \frac{(-1)^n}{(2n+1)} \exp \left[-\frac{(2n+1)^2 \pi^2 F_0}{4} \right] \cos \frac{(2n+1)\pi Z}{2} \right) \quad (3)$$

where C_m is saturated concentration and the equation contains dimensionless parameters as following:

$$F_0 = \frac{Dt}{\delta^2}, \quad Z = \frac{z}{\delta} \quad (4)$$

Equation (3) describes the relative diffusant concentration, which cannot be directly obtained through experiment. Thus, the integration of eq. (3) is performed to obtain the weight gain of immersed sample²³ as follows:

$$\frac{C(z, t)}{C_m} = \frac{M_t}{M_m} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left[-\frac{(2n+1)^2 \pi^2 F_0}{4} \right] \quad (5)$$

where M_t is the mass of diffusant after absorption time of t and M_m is mass of saturated absorption.

A series of PLA specimens were immersed in an organic liquid at various temperatures until saturated. For comparison, two kind of commercial polymers namely Polypropylene (PP) and High Density Polyethylene (HDPE) were also given the same treatment.

The weight gain calculated using eq. (1) is plotted to the immersion time for each material. Figure 1 shows the liquid uptake of three different types of polymer after exposure at room temperature as a function of immersion time. The theoretical curves deduced from Fick's second law expressed in eq. (5) are also plotted in the figure.

The diffusion of the model fluid into all types of polymer approximately follows Fick's law, which shows initial linear increase of weight gain followed by a transition region reaching saturation level at large values of times. Equilibrium plateau is obtained after 120, 168, and 432 h, for Polypropylene, HDPE and PLA-based material, respectively. The saturated weight gains at room temperature immersion for the three polymers can be determined from the equilibrium plateau. It is evident that polypropylene is most sensitive to sorption of this type of organic liquid, with more than 35% weight gain. Highest resistance at room temperature is observed for PLA based biopolymer, which was found to have 2.8% fluid uptake. Weight gain amount of HDPE—the most common material used for application in contact with oxygenated fuel—was 7.5%, a fact also stated by other research.²⁴

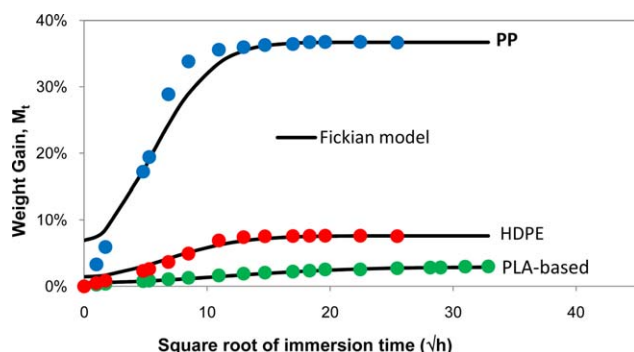


Figure 1. Percentage of fluid uptakes versus square root of immersion time (hours) for all materials at room temperature (the solid line represents the theoretical Fickian weight gain). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Coefficient of Diffusion

The values of diffusion coefficient for all materials immersed at room temperature (20 °C) calculated from the slope of the initial M_t/M_m plot are listed in Table I. That table also presents a comparison of the findings of the present work with the literature values on PLA material exposed to different environment. The order of magnitude of D found here compares well with the values found in the literature; even if they have different characteristics in material and the diffusant.

Effect of Immersion Temperature

When considering service application, it is helpful to study the effect of temperature on the diffusion process. Accordingly, specimens were also immersed in model fluid at 5 °C and 30 °C. The effect of temperature on transport properties of PLA material is shown in Figure 2. Experiment data and its corresponding theoretical Fick's curve fitting are displayed in this figure represented by points and solid line, respectively. The results show progressive increase of weight gain in temperature, with significant increase at 30 °C immersion temperature (5.95%). Smaller increase was observed at lower temperature, achieving equilibrium at 1.90% and 2.91% after 1152 and 1008 hours.

Value of diffusion coefficient is determined by considering the slope of the first part of weight gain curve versus square root of immersion time. It was assumed that diffusion coefficient in the model was independent of time. At initial absorption stage

Table I. Diffusion Coefficient of Selected Polymers Immersed in Various Environment at Room Temperature

Material	Environment	$D \times 10^{-12}$ (m^2/s)
HDPE	Hydrocarbon liquid	3.35
Polypropylene	Hydrocarbon liquid	5.02
PLA: Bioplast GS2189	Hydrocarbon liquid	1.10
PLA: Biomer L9000 ²⁵	Water	2.07
PLA: Cargill Dow 4031D ²⁶	Water vapour, $A_w = 0.9$	0.16
50%PLA/50% Chitosan ²⁷	Water	2.28

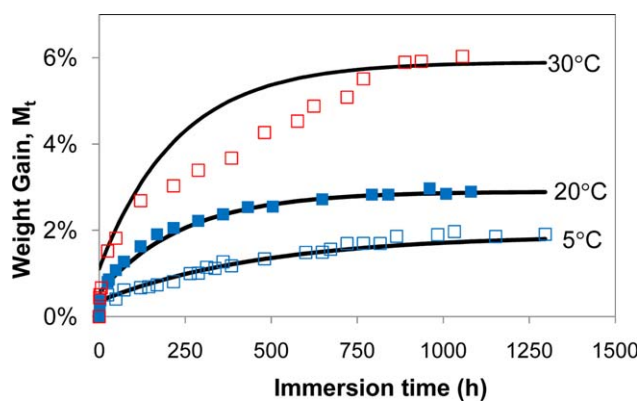


Figure 2. Percentage of weight gain of PLA material versus immersion time at various temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

($M_t/M_m \leq 0.5$), the following equation is used to calculate diffusion coefficient²⁸:

$$\frac{M_t}{M_m} = \int_0^t \frac{2}{\delta} \sqrt{\frac{D}{\pi t}} dt = \frac{4}{\delta} \sqrt{\frac{Dt}{\pi}} \quad (6)$$

where δ is the thickness of the material, M_t is the weight gain at time t and M_m is the saturated weight gain.

Permeability coefficient, P , in $kg\ m\ m^{-2}\ s^{-1}\ Pa^{-1}$ is calculated as

$$P = D.S \quad (7)$$

The values of diffusion coefficient D for samples in different temperature were also calculated using eq. (6) and presented in Table II. This table also exhibits the values of sorption coefficient S , which is taken from the equilibrium plateau of the weight gain curves²⁴ shown in Figure 3. The related permeability coefficient P can be calculated using eq. (7) as an alternative method to measure approximated permeation coefficient which can easily be converted to the substance transmission rate.²⁹

Non-Fickian Diffusion in PLA Material. The experiment data of the model fluid sorption into PLA specimens at diverse temperature levels has been plotted in Figure 2 along with the corresponding theoretical Fick's solution presented in eq. (5). As can be seen in the figure, the phenomenon is observed that at

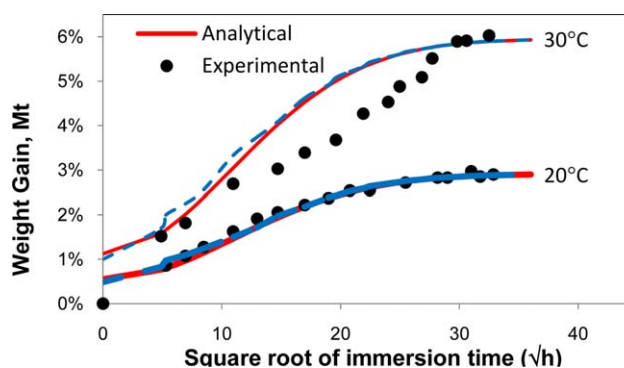


Figure 3. Analytical, experimental data and numerical solution at 20 °C and 30 °C immersion temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. The values of Diffusion (D) and Permeability Coefficient of the Material at Various Environment Temperatures

Immersion temperature	$D \times 10^{-12}$ (m ² /s)	S (g/g)	$P \times 10^{-14}$ (m ² /s)
5 °C	0.57	0.019	1.083
20 °C	1.10	0.03	3.201
30 °C	1.13	0.0595	6.724

5 °C and 20 °C temperature the experiment data agree well with the Fick's Law but there is deviation in the data for higher temperature (30 °C). That means that at high temperature the diffusion behavior of hydrocarbon liquid into PLA material is anomalous and it cannot be adequately described by Fickian diffusion.

Figure 3 clearly shows the anomalous behavior of the liquid sorption at 30 °C compared to that at lower temperature. Results generated from numerical analysis are also shown for both cases. Numerical analysis was carried on using a commercial finite element package, ANSYS Mechanical APDL v. 14. The weight gain is obtained as the average concentration of liquid content within the thickness of the specimen.

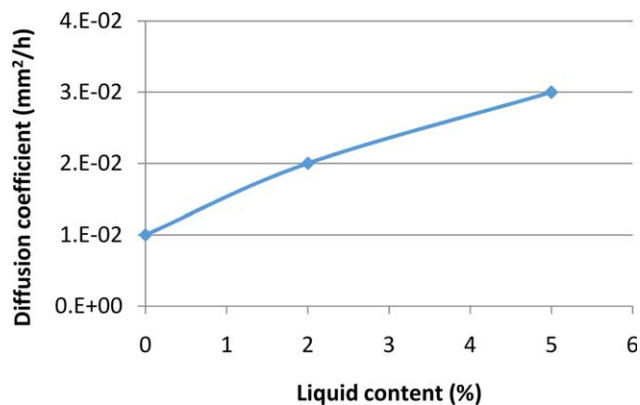
There have been several attempts to recognize and characterize the anomalous sorption in a polymer. It can be characterized by linearly decreasing diffusivity as a function of average liquid content,²⁸ two-stage Fickian process,³⁰ time-dependent function similar to viscoelastic material response and modified Fick's Law with time-dependent diffusion coefficient.³¹

The diffusion coefficient, D , in eq. (2) is assumed to be independent of liquid concentration, C , but this assumption may not be true in the case of non-Fickian diffusion³² and will cause deviation from the classical diffusion behavior. An estimation of diffusion coefficient can be carried out by developing the relation of diffusion coefficient to liquid concentration^{28,32} as given by

$$D = D(C) \quad (8)$$

For the case of liquid diffusion at 30 °C environment temperature as presented in Figure 3, no specific saturation point can be observed thereof, so an estimation of the diffusion coefficient by using Fick's law is not appropriate. The liquid content-dependent diffusion coefficient as shown in eq. (9) is determined by estimating a first value of diffusion coefficient from a virtual saturation level.³² This is repeated for longer immersion time until a relation between diffusion coefficient, D and saturated liquid content C_m can be obtained. Figure 4 shows the relation between D and C_m in the sample, which constructs the liquid content-dependent diffusion coefficient.

In automatically solving the anomalous organic liquid diffusion at high temperature, a finite element code is developed using the FE software, ANSYS Mechanical APDL using the liquid content-dependent diffusion shown in Figure 4. The curves of liquid content to time of absorption with both constant and liquid content-dependent diffusion coefficient, D are plotted in Figure 5. It is shown from the figure that the non-Fickian model displayed in solid line fits better to the experiment data

**Figure 4.** Function of diffusion coefficient with liquid concentration for samples exposed at 30 °C environment temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

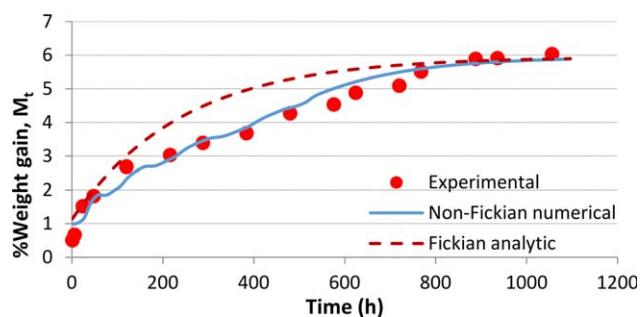
compared to that using Fick's diffusion equation with constant value of D .

Davis^{14,33} has also reported non-Fickian behavior for the diffusion of liquid water as well as water vapour in PLA-based material at 25 °C immersion temperature. The observed anomalous diffusion behavior in PLA was attributed to water diffusion and water-induced polymer relaxation occurring on similar time scales, a fact also confirmed by Loh.³⁴ Non-Fickian behavior may also be the consequences of chemical degradation and sorption-induced microcracks.³⁵ Another mechanism leading to anomalous behavior of liquid absorption could be the swelling of the polymeric material.

Distribution of Liquid Content

The profile of diffused liquid into the material can be obtained by solving the analytical model presented in eq. (3). This section presents an analytical and numerical solution for distribution of fluid diffused into a slab. In this case it is assumed that liquid diffusion is isotropic, that is the same in every direction. Finite element analysis (FEA) is used to numerically calculate the distribution of liquid diffusion with an assumption of constant temperature condition.

The geometry selected to illustrate the fluid diffusion is an infinitive thin plate with thickness (δ) of 1 mm. The material properties of the plate considered correspond to that of the PLA-based material experimentally studied in previous section.

**Figure 5.** Fickian and non-Fickian curve of liquid sorption at 30 °C immersion temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

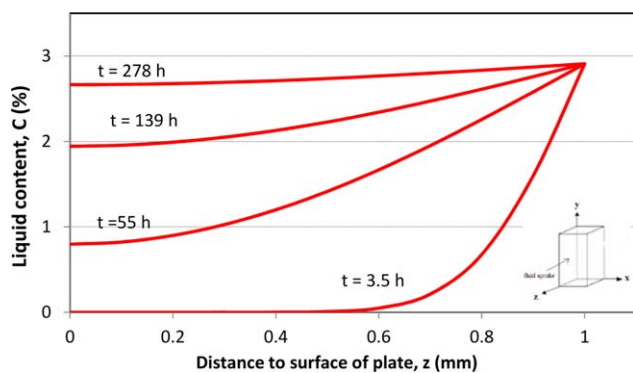


Figure 6. Concentration of liquid within the thickness of a plate from one-side diffusion. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The plate is exposed to fluid environment from one side of the surfaces. The temperature condition is at $T = 20^\circ\text{C}$ and thereby has a diffusion coefficient $D = 1.1 \times 10^{-12} \text{ m}^2/\text{s}$ and saturated fluid uptake $C_m = 2.91\%$. Solution of this case is obtained both analytically and numerically using commercial FEA software.

The evolution of the liquid content before reaching equilibrium concentration can be plotted by using eq. (5). Figure 6 presents varying liquid concentrations with time and position along the thickness of the plate at an application temperature 20°C . In one-side diffusion of 1 mm plate thickness, the specimens will completely saturate in about 429 h. The figure shows the fluid content at 278 h to be at 2.8% weight gain from the initial dry weight throughout the thickness of plate. In one-side diffusion plate, it can be seen that fluid content at the inner side of the plate to be 0.8% at $t = 55 \text{ h}$ and after 139 h it increases to be 1.94%.

In Figure 7, the liquid content at different temperatures at the same value of Fourier number, F_0 , was plotted with position, z . The correspondence time for $F_0 = 0.2$ for environment temperature $T = 5^\circ\text{C}$, 20°C , and 30°C is $t \approx 98, \approx 51$, and 47 h , respectively. It is obvious from these curves that the spatial and time dependence of the liquid content during the diffusion process is affected by the environment temperature.

Using the converged time-step size, the distribution of liquid content of the specimen is numerically obtained and compared

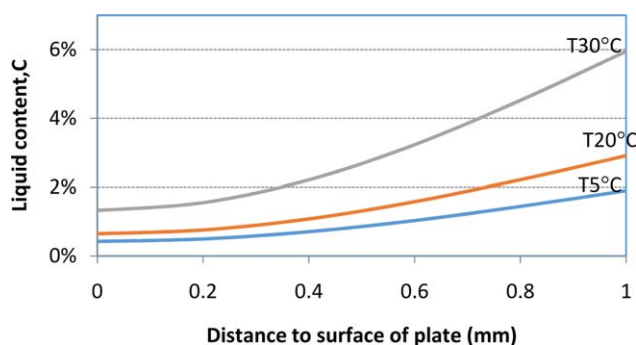


Figure 7. Concentration of liquid inside plate at $F_0 = 0.2$ at various exposure temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

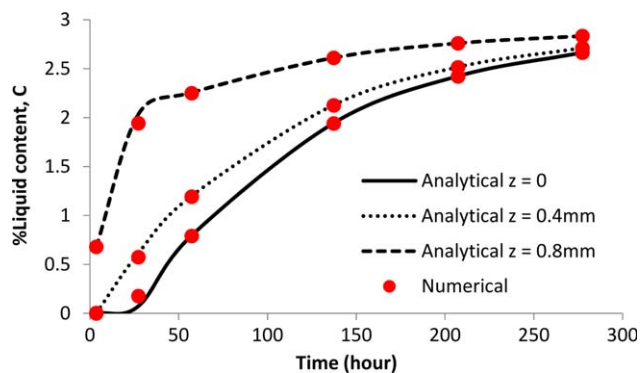


Figure 8. Comparison between analytical and numerical solution of fluid content at different position of z/δ within thickness of plate from one-side diffusion. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

to the analytical solution. The plot of liquid content in different position within the thickness as function of time with surface distance at different time is shown in Figure 8. It can be seen that the analytical and numerical solution using FEA method agrees well in the case of diffusion within a rectangular plate.

The graphical representation of the fluid content profile for various times of observation during immersion period along the thickness is generated using the ANSYS Workbench 14.0 and is shown in Figure 9.

Using similar geometry of plate with thickness 1 mm, consider a plate conditioned at temperature $T = 30^\circ\text{C}$, which has liquid content-dependent diffusion coefficient. The numerical analysis is performed to obtain the distribution of liquid content for this case and displayed in Figure 10. A different profile with the case of Fickian diffusion shown in Figure 6 was observed.

In this section, it has been presented that the liquid content within the material is distributed non-uniformly as function of time and position. The material is submitted to nonuniform distribution over an extended period before reaching a saturated condition, much more slowly than temperature because of the slow movement of liquid.³⁶ Initially, a higher liquid concentration is present near the surface at which the absorption occurs more rapidly rather than in the inner layers and then the material moves toward equilibrium liquid concentration as time passes. It comes to a consequence, where property changes associated with the presence of liquid are not uniformly distributed within the material.³⁷

Mechanical Properties

This section presents the result of experimental testing on the mechanical properties of the PLA-based material before fluid immersion and after achieving saturated liquid content. As discussed previously in Section 1, many studies have focused on the effect of water/moisture sorption on mechanical properties and evaluating the evolution of mechanical properties with time. In this article, however, measurement of mechanical properties was performed after it has reached or gets near to equilibrium. It is expected that the fluid uptake has uniformly distributed in the material and can be properly analyzed.²¹ Therefore, the dependency of mechanical properties on liquid

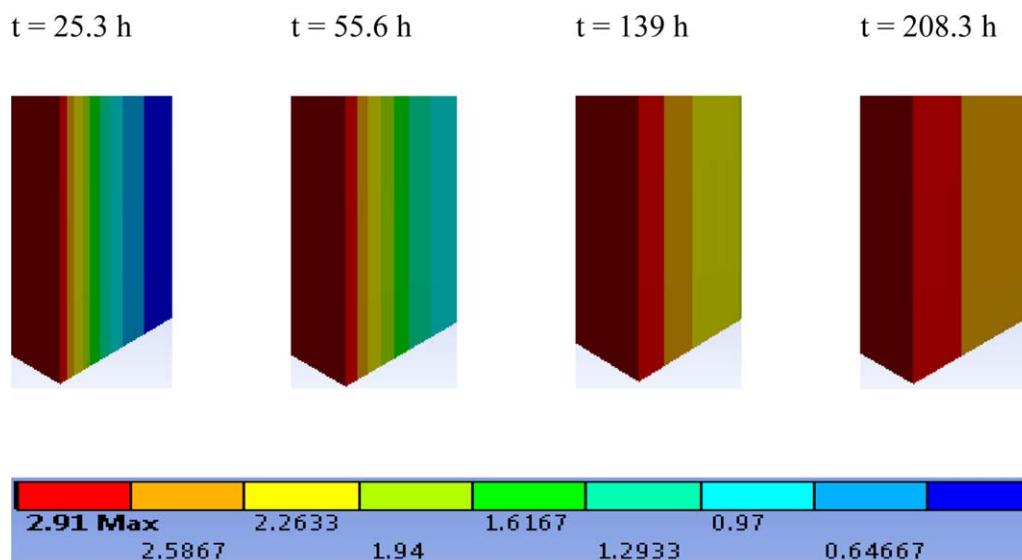


Figure 9. Profile of liquid content obtained from the FEA software at various exposure times. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

content was examined by measuring the properties of saturated specimens conditioned in different temperature levels. In other words, varying levels of liquid content was obtained by accelerating the level of liquid absorption through different immersion temperatures.

Tensile Properties

This section reviews the experimental results of measured tensile properties and their relation to liquid content. The tensile properties evaluated are tensile strength, modulus, strain at break, and strain at maximum stress. Figure 11 shows the average value of tensile properties for the PLA-based material at various levels of liquid concentration. It can be seen that the tensile strength decreases progressively as a function of liquid uptake, from 35 MPa in dry specimen to almost 12 MPa in specimen with 5.95% of liquid content. The elastic modulus and tensile strength are observed to be linearly dependent on the liquid content with a strong correlation coefficient.

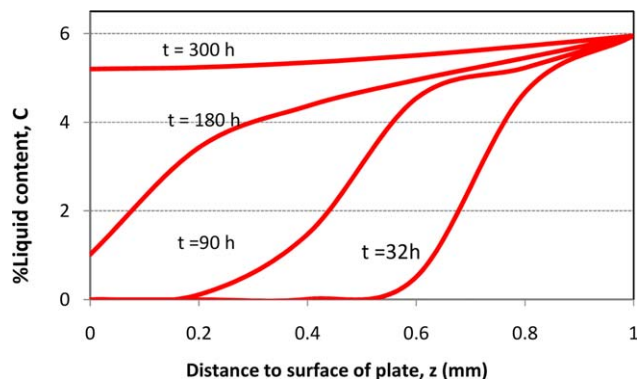


Figure 10. Concentration of liquid within the thickness of a plate from one-side non-Fickian diffusion. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Flexural Properties

The flexural tests performed measured properties such as flexural strength, modulus, elongation at break and elongation at maximum stress. Figure 12 summarizes the flexural test results for the PLA-based material at various levels of fluid concentration which show the trends in flexural modulus and flexural strength. The figure shows that the flexural strength decreases with the liquid content, with a decrease of 30% from 30 MPa in increasing 5.95% of liquid uptake. Linear relations exist but with lower correlation coefficient compared to that in tensile properties. The decreasing of flexural strength with increasing sorption amount is in agreement with other researches, which investigated the performance of PLA material in contact with liquid water³⁸ and in high humidity conditions.⁴

Impact Properties

The impact test is performed to determine the resistance of the material and the amount of energy it is capable of absorbing. The impact property which determines the toughness of the material was measured following the ASTM standard. The measured notched impact strength of dry PLA material, with a value of 1.67 kJ/m², has comparable result with the result

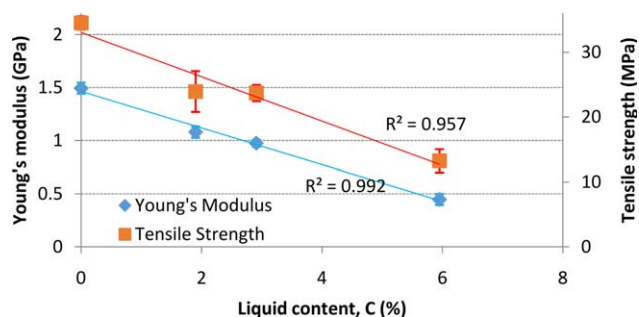


Figure 11. Linear relation of elastic modulus and tensile strength with fluid uptake. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

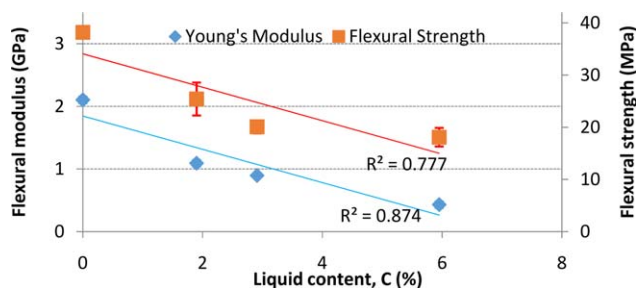


Figure 12. Exponential relation of flexural modulus and strength with fluid content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

reported by.³⁹ The impact strength measured from the recorded energy absorbed of specimens with different levels of liquid content are given in Figure 13.

The impact test result presented in Figure 13 shows different trend when compared to results of the tensile and flexural strength. As the liquid content increased, higher value of absorbed energy was observed after fracturing the specimens. However, after reaching maximum value of 2.7 kJ/m² in specimen with 2.91% liquid content, the impact strength of specimen with 5.95% liquid content declined to 2.1 kJ/m². This behavior probably relates to significance degradation experienced by the high liquid concentration-material, as was also observed for PLA samples exposed to liquid water by.³⁸

CONCLUSIONS

This article has reported a systematic investigation of sorption of an organic liquid into a PLA-based material. The experiment results confirm the time-dependent liquid sorption, which is highly influenced by the surrounding temperature. At low temperature, the kinetics of liquid sorption follows the Fick's law but at higher temperature, it showed a deviation from the Fickian curve. The anomalous diffusion can be associated with extensive swelling reported at high conditioned temperature.

Based on the diffusion parameters obtained experimentally, analytic and numerical solutions were obtained to determine the distribution of liquid content within the thickness of material. Conformity with the theoretical solution in the problem of sim-

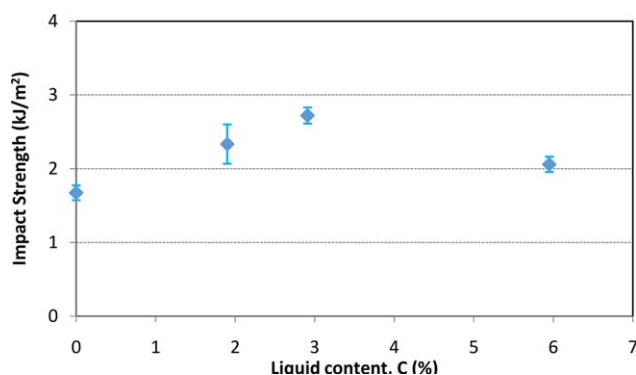


Figure 13. Impact strength of PLA-based specimen as a function of liquid concentration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ple geometries motivates to employ the FE analysis in modelling of diffusion process into more complex design. The liquid uptake in the material distributed nonhomogeneously as a function of time and position.

It also confirms a significant impact of liquid absorption on mechanical properties of PLA-based material through the measurement of static and dynamic properties. The response of this material to liquid absorption was consistent with other reports^{4,24,40–42} on various types of polymeric material in contact with various liquid environments. The decrease in mechanical properties could be enhanced by both degradation and organic liquid sorption. Those reports suggested that the mechanical response because of liquid sorption was similar to the effect of temperature. The results show progressive decrease of the modulus and strength by increasing of fluid content inside the material. The increase of elongation was observed indicating plasticizing effect of fluid exposure on the PLA-material. The dependency of property changes with liquid content leads to inhomogeneous properties inside the material. Since liquid content distribution is a function of time and position, the material is generally submitted to nonuniform distributions of liquid content over an extended period before reaching a saturated condition.

ACKNOWLEDGMENTS

One of the authors (Widiastuti) thanks Indonesian Directorate General of Higher Education (DIKTI) for the fellowship awarded

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