

Antioxidant Deterioration in Active Composite Film During Storage

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ABSTRACT

Pure polyactic acid is widely used for packaging, but it has limitation due to its oxygen barrier property. We investigated oxygen scavenging active packaging by incorporating synthetic antioxidant butylated hydroxyl toluene (BHT) into matrix composite film (plasticized polylactic acid-natrium montmorillonite/ NaMMT) using direct casting. The 2,2-Diphenyl-1-picrylhydrazyl (DPPH) or antiradical activity was used to investigate oxygen scavenging of butylated hydroxytoluene in PLA active composite film during 15 storage days at 30°C. Oxygen permeability was calculated by using ASTM F3136-15 method. BHT Oxidation rate of the active film composite film was 0.043 times per day. The BHT was estimated fully deteriorate after 108 storage days. The research revealed that the oxygen barrier property improved by 2.3 times compared to the passive polylactic composite film. BHT concentration between 5-10% was enough to significantly reduce oxygen permeability value. Oxygen permeability value and antiradical activity deterioration was significant correlated at 97 to 99 percents.

KEY WORDS

antiradical, butylated hydroxy toluene (BHT), oxygen permeability oxygen scavenging, polylactic acid (PLA)

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1. INTRODUCTION

The purpose of primary packaging design for food is to prevent oxygen permeation by diffusion through the film packaging structure during storage. Recently, active film packaging design has become an interesting research, especially when related to the incorporated active material in the matrix polymer film. Polylactic acid (PLA) is an interesting biopolymer matrix film material that be applied as oxygen scavenging active film. This material is a versatile entirely produced from renewable resources [1] and have interested since concern for the minor environment impact in disposal packaging [2].

Gas barrier property is becoming an important variable to address when designing a good packaging system. PLA has a drawback as oxygen barrier property less than other plastic material such as polyethylene terephthalate (PET) [3]. In order to decrease oxygen permeability was also executed by blending PLA with other polymers such as compatible plasticizer [4-5] ; poly(caprolactone) [6], chitosan [7] and polyethylene glycol [8-9]. Furthermore, introducing clay fillers that were based on PLA matrix composite film packaging were also applied to enhance the oxygen barrier properties [10]. Composite film consisting of plasticized PLA and natrium montmorillonite improved the oxygen barrier properties by 80% due to tortuous path formation in the composite structure [11].

An improved oxygen barrier property film packaging can be developed by incorporating antioxidant material into the composite film matrix. An antioxidant acting as an oxygen scavenger has the role of eliminating oxygen volumes which permeate through the packaging or the head space [12]-13]. Incorporating an oxygen scavenger agent into the polymer material within the packaging film provides some benefits, such as its suitability for the food packaging system. It

is also safe for consumers by eliminating food product rejection and reduces cost production. Researchers have shown an increased interest surrounding the incorporation of oxygen scavenger materials into packaging materials [14].

Among the antioxidant materials, butylated hydroxytoluene (BHT) is an example of one commonly used in plastic, pharmaceutical, and food industries as an antioxidant agent. BHT releases a hydrogen agent to free radicals, resulting in more stable compounds [15]. Some researchers had reported that though applying BHT for packaging film into PLA decreased the glass temperature and crystallinity, it had the positive effect of improving oxygen permeability. Unfortunately, the concentration BHT should be less than 10% due to the separation phase indication [16]. Meanwhile, releasing incorporated BHT in PLA film at a lower concentration (0.79%) into coconut oil provided no changes within the thermal properties, oxygen, and water vapor permeability [15].

Incorporating synthetic phenolic antioxidant (SPAs) including BHA, BHT, PG and TBHQ to PLA films at 1% (w/w) improved the oxygen permeability by 30% although the water vapor permeability did not change [17]. It has been cleared that an oxygen scavenger active film based on PLA and BHT design improved the oxygen permeability and antioxidant release. However, the previous research only addressed the incorporation of BHT into neat PLA for active film design, since the NaMMT was proven able to enhance the oxygen barrier property for composite film based on plasticized PLA matrix [11]. However, there is no report relating to the oxygen scavenging active film based on plasticized PLA composite filled NaMMT.

Furthermore, measuring the active film oxygen scavenging performance can be accomplished by using 2,2-Diphenyl-1-picrylhydrazyl (DPPH) method. The DPPH is the most popular measurement method relying on radical scavenging activity

which is based on the reaction between the DPPH with the antioxidant [18]. Then, oxygen transmission rate (OTR) will be measured to ensure the addition of BHT into the oxygen permeability active film composite PLA-NaMMT. A new method, OTR investigation, was applied that was based on dynamic accumulation method [19].

This research aimed to investigate the improvement of oxygen permeability and oxygen scavenging active film based on plasticized PLA –NaMMT composite. Antioxidant activity was measured using DPPH analysis and oxidized BHT rate was calculated from empirical. Then, the oxygen permeability was calculated from the oxygen transmission rate and used to measure the prolongation active film period. This research also deals with the antiradical activities and oxygen permeability improvement.

2. EXPERIMENTAL SECTION

2.1 Material

Poly(lactic acid) (PLA) A-101 with 80,000 g/mole and density 1.24 g/cm³ was supplied from Shenzhen Esun (China). Then, a chloroform HPLC grade C606-4 was purchased from Fisher Scientific, USA. Polyethylene Glycol-400 was supplied from Fisher Scientific, USA with an average molecular weight 380-420, density 1.13 g/mol. Unmodified montmorillonite (Na-MMT) was purchased from southern clay products, Gonzales, Texas, USA. 1,1-diphenyl-2-picryl-hydrazyl (DPPH) was purchased from Sigma-Aldrich (USA), methanol was purchased from Merck (Germany) and butylated hydroxytoluene (BHT) was purchased from Sigma-Aldrich (USA).

2.2 Methods

Active film composite consisting of matrix composite (PLA-PEG400-NaMMT) and antioxidant agent BHT was prepared using direct casting

method [20]. Before processing, PLA was dried in the oven for 6 hours at 45°C. Plasticized PLA was produced from a PLA-PEG400 solution under chloroform solvent. Amount of PLA was 5% weight of chloroform (w/v) and PEG400 5% weight of PLA (v/w). In detail, 20 g PLA were dissolved in 400 ml chloroform and stirred vigorously at 750 rpm for 60 minutes at 55°C. Then, PEG was added at about 1.13 ml into PLA solution and continued to be stirred for 15 minutes. Next step, composite matrix solution was created by adding NaMMT 5% of PLA (w/w) or 1 g NaMMT into plasticized PLA solution and stirred for 15 minutes. Finally, BHTs were introduced in the composite solution at various concentrations of 1%, 5% and 10% of PLA (w/w) and stirred for 15 minutes. The dissolved active film composite solution were poured onto a glass petridish with a 10 cm diameter. Then, active composite solutions on the petridishes were dried into films at 35°C for 15 hours. Resultant active film composite plasticized PLA-NaMMT-BHT were peeled from petridishes and the active film thicknesses were measured in 7 locations using a micrometer with thickness $25 \pm 1.8 \mu\text{m}$.

2.3 Oxygen Permeability Measurement in various temperature

The oxygen permeability of the matrix film composite plasticized PLA-NaMMT and oxygen scavenging film composite plasticized PLA-NaMMT-BHTs were measured according to a new method called “dynamic accumulation” by measuring the oxygen transmission rate. This OTR measurement was based on ASTM F3136-15 [21] that utilized permeation apparatus from Oxsense, Inc. 6000 South Eastern Ave, Suite 14G, Las Vegas, NV 89119, USA. The oxygen accumulation chamber had a sample area of 16.62 cm² and a volume of 8.3 cm³. Initially, the cell was purged with more than 10 volumes of industrial grade compressed nitrogen. The completion of the purge was followed by monitoring oxygen concentration decrease to a constant

zero level using the OxySense Model 310 device. Thus, industrial-grade oxygen (approximately 100%) was used to purge the test-gas chamber. Oxygen concentration in the dynamic accumulation (DA) chamber was measured and recorded periodically during the test using commercially available oxygen fluorescence sensor (Model 310; OxySense, Inc). OTR was subsequently calculated as described [19]. The controlled temperature chamber measurement used a mini refrigerator (NuCool C-RNU281VS; Haier America Trading, LLC, NY, USA). A Light bulb was applied by a PID heat controlled (Omega CSC32; Omega Engineering, INC, Stamford, CT, USA). Temperature control was set into certain temperature (15°C; 23°C and 30°C as experimental variables). The PID controller temperature measurement deviated at approximately 0.2°C. In this research, the oxygen transmission rate was measured at differences temperatures, which are listed as follows: 15°C, 23°C and 30°C. All OTR measurements were replicated 3 times.

2.4 Antiradical Activity

The DPPH radical scavenging activity was conducted according to [22] with a slight modification. A piece of active film plasticized PLA- (0.1 g) was cut into small pieces and mixed with 2 ml methanol. The mixture was vigorously vortexed for 3 minutes and placed in a dark environment at room temperature for 3 hours. Then, it was vigorously vortexed for 3 minutes and centrifuged at 2300 rpm for 10 minutes. The supernatant was analyzed for DPPH radical scavenging activity. An aliquot of methanol extract (500µl) was mixed with 2 ml of 0.06 mM DPPH in methanol. The mixture was vigorously vortexed for 1 minute and allowed to stand at room temperature in the dark for 30 minutes. The absorbance was measured at 517 nm using UV spectrometer (Model UV-2101 PC, Shimadzu, MD, USA). The methanol was used as control was calculated and mixed with 0.12 mM DPPH. Then, DPPH radical

scavenging activity was calculated as follows

$$\text{Radical scavenging activity (\%)} = \left(1 - \frac{A_{\text{sample}}}{A_{\text{control}}} \right) \times 100\%$$

Where A_{sample} is the absorbance of sample and A_{control} is the absorbance of the control. The values presented were the average of three replication measurements.

3. RESULT AND DISCUSSION

3.1 Oxygen Permeability

Oxygen permeability property film packaging relies on quantification of oxygen transmission through the film packaging. Packaging material has a lower oxygen permeability coefficient indicates the oxygen pressure inside the packaging falls to very low the value that affects the extending product shelf-life [23]. Additionally, packaging design purposes improving oxygen barrier property that shown lower oxygen permeability coefficient. In this research, the role of oxygen permeability value of PLA active films composite added with BHT. Oxygen permeability active film PLA composite in different temperature measurements are shown in Fig 1.

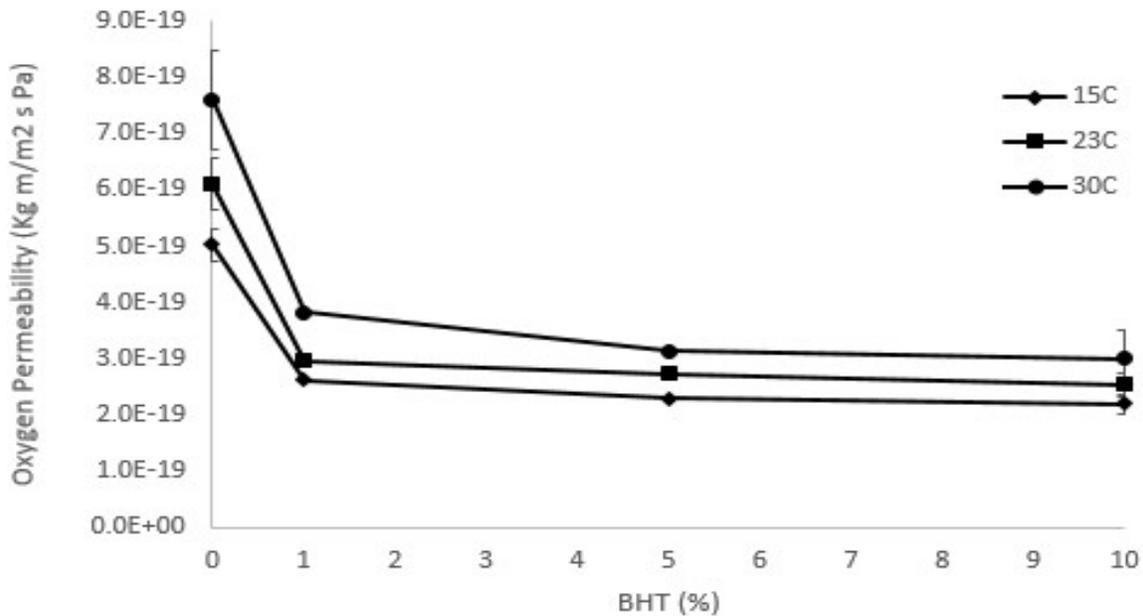


Figure 1. Oxygen permeability active film based on PLA.

In Fig. 1, a lower oxygen permeability value indicates small oxygen molecules can through pass the film. This research has identified that introducing a larger BHT into plasticized PLA matrix composite resulted in a significantly lower oxygen permeability value. This finding proved that presenting BHT in active film PLA composite inhibited oxygen diffusion through the film. Incorporated BHT into PLA film was reported improving packaging film from CO₂ and O₂ permeation although are strongly affected on the quantity antioxidant added [1].

Measured oxygen permeability containing antioxidants are shown in Fig. 1, presenting BHT reduced oxygen permeability value and did not significantly change the plasticized PLA-NaMMT matrix oxygen permeability coefficient. The oxygen permeability plasticized PLA-NaMMT-BHT active films reduced at 2.0, 2.4, and 2.5 times when introduced BHT 1%, 5% and 10%, respectively. Reducing the oxygen permeability value indicates improving oxygen barrier or permeation. In addition, correlation of BHT breakdown

and the oxygen permeability reduction was calculated between 0.97 and 0.99. It means that the BHT has proved to enhance the oxygen barrier properties of oxygen scavenging active film composite plasticized PLA.

Furthermore, this research also measured the effect of temperature to oxygen permeability performance on active film plasticized plasticized PLA-NaMMT-BHT. Increasing the temperature accelerated oxygen diffusion through the active film plasticized PLA composite (Fig 1). As expected, oxygen permeability value tended to increase when a higher temperature was applied during measurement. Temperature dependence on oxygen permeability can be processed using Arrhenius equation to find the activation energy.

Table 1. Activation energy and pre-exponential factor oxygen permeability active film composite plasticized PLA-BHT

Active Film Composite	Energy activation (kJ/mol)	Pre exponential factor (x10 ³)
Plasticized PLA-NAMMT+BHT 0%	13.31	597.2
Plasticized PLA-NAMMT +BHT 1%	8.59	5.4
Plasticized PLA-NAMMT +BHT 5%	7.42	1.6
Plasticized PLA-NAMMT +BHT 10%	7.29	1.5

Activation energy can be generated by plotting graph between reciprocal temperature and Ln oxygen permeability. Table 1 presents the activation energy oxygen permeability as a function of BHT concentration. In this table, it is clear that the activation energy was lower following an increase in BHT concentration in the matrix film composite plasticized PLA. Activation energy is lower indicated oxygen barrier property improvement or a decreasing oxygen permeability value [24]. However, introducing BHT into PLA matrix film composite between 5% and 10% did not significantly affect the oxygen permeability in storage temperature between 15-30°C. The BHT threshold was at 5% amount during PLA active film composite to improve oxygen barrier property.

3.2 Antiradical Activity

DPPH was used to investigate the antiradical activity of BHT in the active film composite to represent oxygen scavenging performance. The antiradical activity BHT in various concentrations were observed for a 15 days period. The storage system was conditioned, omitting environmental effect using insulated storage that maintained the storage at a desired temperature of 30°C. The BHT deteriorations were ensured from the free oxygen which was present in the chamber during storage.

This research applied a control film consisting of PLA-PEG400-NaMMT-BHT 0% or matrix film composite without any BHT addition. From

the measurement, the DPPH investigation showed neither antiradical activity nor oxygen scavenging activity. As expected, lack of BHT into matrix film composite can be categorized as a passive composite film. The radical scavenging activity result of the active film composite (PLA-PEG400-NaMMT-BHT) were displayed in Figure 2.

One interesting finding in this research is the fact that all active films composite provided antiradical activity during storage which enhances the theory of BHT as a single agent oxygen scavenger. This research revealed that antiradical activity tended to decrease the longer the storage time. Surprisingly, incorporating BHT 1% into PLA film composite expressed significant oxygen scavenging activity rate that could be oxidized rapidly by free oxygen present in the chamber. The figure 2, showed a significant antiradical activity beginning from the fourth day of storage.

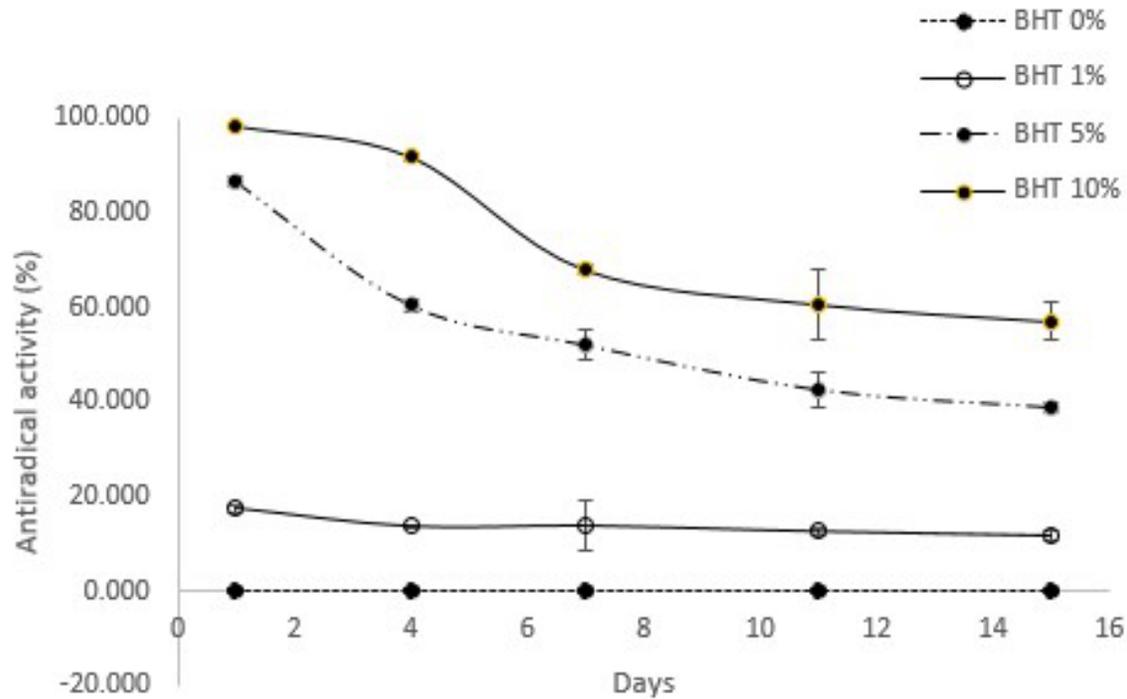


Figure 2. Antiradical activity active film PLA composites

Another important finding was that incorporating BHT into plasticized PLA film without the addition of NaMMT ensued a better oxygen scavenging than the active film which consisted of lower BHT concentration. It seems that the oxidative retention is affected by BHT concentration. The data indicated remaining antiradical activity PLA film composite-BHT 5% was lower than PLA film-BHT 10%. The antioxidant addition occurred less free volume than a pure matrix film that resulted lower oxygen permeation through pass the film packaging [25]. In this research, diffused oxygen through free volume of the plasticized PLA-NaMMT matrix film will interact with and oxidized BHT continuously. A higher BHT concentration in the matrix film offered larger antioxidant that acted reducing as oxidation process and ensure antioxidant activity.

The most interesting finding was when presenting BHT 10% into plasticized PLA matrix filled NaMMT showed a higher remaining BHT among others. It means that the largest amount of BHT provided a longer period retention to oxidize from free oxygen in the ambient. However, detailed explanation could be correlated with the existing of MMT in the active film. Previously, our research revealed introducing NaMMT into plasticized PLA impact to reduce the oxygen barrier properties due to tortuous path configuration. NaMMT configures a tortuous path which increased the diffusion distance of oxygen passing through the film at about 28% [11].

BHT degradation trend showed exponentially both in the oxygen scavenger active film based on PLA filled with and without NaMMT. Other researchers reported the first order degradation of BHT occurred when it was applied into HDPE [26] Oxidized BHT rate grew faster whilst the amount

of BHT in the matrix plasticized PLA was getting smaller. The BHT oxidation rate was minimalized at 10% with a rate of -0.043 times per day. Then, a faster BHT degradation rate was achieved -0.097 times per day that presented about 1% BHT incorporated in the matrix film. Furthermore, BHT will be totally loss in the matrix film composite plasticized PLA-NaMMT within 23, 15 and 10 days of presenting BHT 10%, 5% and 1%, respectively at 30°C. The BHT loss rate was better than HDPE-BHT, which lost about 95% within 7 days of 30°C storage (Han et al., 1987) and disappeared within 5 days of storage at 45°C [26]

CONCLUSION

We have confirmed that BHT is an antiradical agent that improves oxygen barrier active film composite. The use of a higher concentration of BHT in the matrix film composite results in significant antiradical activity and oxygen scavenging improvement, but a decrease in antiradical activity during storage the period. The BHT retention rate is slower when a larger amount incorporated into the matrix film composite. The antiradical activity remained at 57% during the 15 days and was predicted to disappear after 108 days storage at 30°C. BHT enhances oxygen barrier active film composite by about 2.7 times and reduces oxygen permeability at -0.043 kg m/m² s Pa times per day. This research concluded that introducing BHT at 5% and 10% did not result significantly to oxygen permeability. Temperature effects oxygen diffusion through the active film of plasticized PLA composite. The improvement of the oxygen barrier property correlates with the BHT breakdown and the oxygen permeability reduction of 0.97-0.99%.

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REFERENCES

- [1] C. M. B. Gonçalves, L. C. Tomé, H. Garcia, L. Brandão, A. M. Mendes, and I. M. Marrucho, *Effect of natural and synthetic antioxidants incorporation on the gas permeation properties of poly(lactic acid) films*, vol. 116, no. 2. Elsevier Ltd, 2013.
- [2] L. Avérous and E. Pollet, “Biodegradable Polymers,” in *Environmental Silicate Nano-Biocomposites*, London: Springer-Verlag, 2012.
- [3] R. Auras, B. Harte, and S. Selke, “An Overview of Polylactides as Packaging Materials,” pp. 835–864, 2004, doi: 10.1002/mabi.200400043.
- [4] K. Yuniarto, Y. A. Purwanto, S. Purwanto, B. A. Welt, K. Purwadaria, and T. C. Sunarti, “Thermal Properties , Crystallization and Oxygen Permeability Plasticized Poly (Lactic acid) Film Reinforced Na-Montmorillonite,” *Makara J. Technol.*, vol. 20, no. 1, pp. 1–6, 2016, [Online]. Available: journal.ui.ac.id/technology/journal/article/view/3048.
- [5] K. Yuniarto and C. Irawan, “Morphological , Thermal and Oxygen Barrier Properties Plasticized Film Polylactic Acid Morphological , Thermal and Oxygen Barrier Properties Plasticized Film,” vol. 9, no. 3, 2017.
- [6] M. E. Broz, D. L. VanderHart, and N. R. Washburn, “Structure and mechanical properties of poly(D,L-lactic acid)/poly(ϵ -caprolactone) blends,” *Biomaterials*, vol. 24, no. 23, pp. 4181–4190, 2003, doi: 10.1016/S0142-9612(03)00314-4.
- [7] Y. Wan, H. Wu, A. Yu, and D. Wen, “Biodegradable polylactide/chitosan blend membranes,” *Biomacromolecules*, vol. 7, no. 4, pp. 1362–1372, 2006, doi: 10.1021/bm0600825.
- [8] R. M. Rasal, A. V Janorkar, and D. E. Hirt, “Progress in Polymer Science Poly (lactic acid) modifications,” *Prog. Polym. Sci.*, vol. 35, no. 3, pp. 338–356, 2010, doi: 10.1016/j.progpolymsci.2009.12.003.
- [9] K. Yuniarto, B. A. Welt, A. Purwanto, H. K. Purwadaria, and A. Abdellatif, “Effect of Plasticizer on Oxygen Permeability of Cast Polylactic acid (PLA) Films Determined using Dynamic Accumulation Method,” *J. Appl. Packag. Res.*, vol. 6, no. 2, pp. 51–57, 2014.
- [10] N. Bitinis, R. Verdejo, E. M. Maya, E. Espuche, P. Cassagnau, and M. A. Lopez-manchado, “Physicochemical properties of organoclay filled polylactic acid / natural rubber blend bionanocomposites,” *Compos. Sci. Technol.*, vol. 72, no. 2, pp. 305–313, 2012, doi: 10.1016/j.compscitech.2011.11.018.
- [11] K. Yuniarto, Y. A. Purwanto, S. Purwanto, B. A. Welt, H. K. Purwadaria, and T. C. Sunarti, “Thermal Properties, Crystallinity, and Oxygen Permeability of Na-montmorillonite Reinforced Plasticized Poly(lactic acid) Film,” *Makara J. Technol.*, vol. 20, no. 1, p. 1, 2016, doi: 10.7454/mst.v20i1.3048.
- [12] A. L. Brody, E. R. Strupinsky, and L. R. Kline, *Active Packaging for Food Applications*. Boca Raton: CRC Press, 2001.

- [13] H. M. C. de Azeredo, "Nanocomposites for food packaging applications," *Food Res. Int.*, vol. 42, no. 9, pp. 1240–1253, 2009, doi: 10.1016/j.foodres.2009.03.019.
- [14] M. A. Busolo, S. Torres-giner, and J. M. Lagaron, "Enhancing the Gas Barrier Properties of Polylactic Acid by Means of Electrospun Ultrathin Zein Fibers," in *ANTEC*, 2009, pp. 2763–2767.
- [15] H. Ortiz-vazquez, J. Shin, H. Soto-valdez, and R. Auras, "Release of butylated hydroxytoluene (BHT) from Poly (lactic acid) films," *Polym. Test.*, vol. 30, no. 5, pp. 463–471, 2011, doi: 10.1016/j.polymertesting.2011.03.006.
- [16] C. M. B. Gonçalves, L. C. Tomé, H. Garcia, L. Brandão, A. M. Mendes, and I. M. Marrucho, "Effect of natural and synthetic antioxidants incorporation on the gas permeation properties of poly (lactic acid) films," vol. 116, pp. 562–571, 2013, doi: 10.1016/j.jfoodeng.2012.12.034.
- [17] M. Jamshidian, E. Arab, M. Imran, M. Javeed, F. Cleymand, and S. Desobry, "Structural , mechanical and barrier properties of active PLA – antioxidant films," *J. Food Eng.*, vol. 110, no. 3, pp. 380–389, 2012, doi: 10.1016/j.jfoodeng.2011.12.034.
- [18] A. L. Dawidowicz, D. Wianowska, and M. Olszowy, "On practical problems in estimation of antioxidant activity of compounds by DPPH Å method (Problems in estimation of antioxidant activity)," *Food Chem.*, vol. 131, no. 3, pp. 1037–1043, 2012, doi: 10.1016/j.foodchem.2011.09.067.
- [19] B. A. Abdellatief, Ayman; Welt, "Comparison of New Dynamic Accumulation Method for Measuring Oxygen Transmission Rate of Packaging against the Steady-State Method Described by ASTM D3985," *Packag. Technol. Sci.*, vol. 26, no. 5, 2012, doi: 10.1002/pts.1974.
- [20] C. Yuniarto, Kurniawan; Bruce A Welt; Foliatini; Hanafi; Irawan, "Morphological , Thermal and Oxygen Barrier Properties Plasticized Film Polylactic Acid Morphological , Thermal and Oxygen Barrier Properties Plasticized Film," *Appl. Packag. Res.*, vol. 9, no. 3, pp. 1–9, 2017.
- [21] ASTM, "Standard Test Method for Oxygen Gas Transmission Rate through Plastic Film and Sheeting using a Dynamic Accumulation Method 1," *Astm*, pp. 1–7, 2015, doi: 10.1520/F3136-15.2.
- [22] A. Jongjareonrak, S. Benjakul, W. Visessanguan, and M. Tanaka, "ARTICLE IN PRESS Antioxidative activity and properties of fish skin gelatin films incorporated with BHT and a -tocopherol," vol. 22, pp. 449–458, 2008, doi: 10.1016/j.foodhyd.2007.01.002.
- [23] V. Siracusa, "Food packaging permeability behaviour: A report," *Int. J. Polym. Sci.*, vol. 2012, no. i, 2012, doi: 10.1155/2012/302029.
- [24] K. Komatsuka, Tomomi, Nagai, "Temperature Dependence on Gas Permeability and Permselectivity of Poly (lactic acid) Blend Membranes R ;," vol. 41, no. 5, pp. 455–458, 2009, doi: 10.1295/polymj.PJ2008266.

- [25] Y. Byun, Y. T. Kim, and S. Whiteside, "Characterization of an antioxidant polylactic acid (PLA) film prepared with a -tocopherol , BHT and polyethylene glycol using film cast extruder," *J. Food Eng.*, vol. 100, no. 2, pp. 239–244, 2010, doi: 10.1016/j.jfoodeng.2010.04.005.
- [26] J. Lee, N. Koo, and D. B. Min, "Reactive Oxygen Species, Aging, and Antioxidative Nutraceuticals," *Compr. Rev. Food Sci. Food Saf.*, vol. 3, no. 1, pp. 21–33, 2004, doi: 10.1111/j.1541-4337.2004.tb00058.x.