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EFFECT OF THERMOPLASTIC POLYESTER ELASTOMER CONTENTS ON GAS PERMEABILITY OF LOW DENSITY POLYETHYLENE BASE MODIFIED ATMOSPHERE PACKAGING

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Abstract

Modified atmosphere packaging (MAP) is a method to passively adjust O_2 and CO_2 concentration inside the package. The gas composition will change over time due mainly to the respiration rate of fresh food or produce inside the packaging and the permeability of the packaging film. The atmosphere with richer CO_2 and poorer O_2 can reduce the respiration rate of fresh food or produce and consequentially prolong their shelf lives. However, to achieve the desired level of O_2 and CO_2 concentration within reasonable time for particular food or produce, the packaging film must have suitable gas permeabilities. In this study, new MAP films were produced from blend between low density polyethylene (LDPE) and thermoplastic polyester elastomer (TPEE). Melt blending and film casting were done using twin screw extruder and cast film extruder, respectively. The contents of TPEE were varied from 10 to 50 wt%. Under stretching condition during cast film process and weak interfacial adhesion between LDPE and TPEE, small pores were created in the MAP film resulting in higher oxygen and water vapor transmission rates than neat LDPE film. The oxygen transmission rate (OTR) of MAP film, measured following ASTM D3985, was found to increase with increase in TPEE contents and the highest OTR was obtained from neat TPEE. Because TPEE is an elastomer with high flexibility and free volume, O_2 can easily diffuse through its free volume. The results of water vapor transmission rate (WVTR) of MAP film, measured following ASTM E398-03, showed that WVTR of MAP film from neat TPEE was higher than that of neat LDPE. Increasing TPEE contents caused WVTR of MAP film to be increased because water vapor can easily diffuse through the free volume in TPEE. The thermograms from a differential scanning calorimeter (DSC) revealed that MAP film from neat TPEE had percent crystallinity (%Xc) lower than those of other MAP films. At low TPEE contents, TPEE is a nucleating agent for LDPE matrix which increases %Xc of MAP film. These results demonstrated that the MAP films from blend between LDPE and TPEE can be tailored to provide proper gas and water vapor permeability suitable for use as MAPs for fresh food and produce.

Keywords: MAP, Modified atmosphere packaging, Low density polyethylene, Thermoplastic polyester elastomer

Introduction

Eating fresh fruits and vegetables daily provides many health benefits including the prevention of illnesses [1] because fresh fruits and vegetables contain various vitamins and good bioactive compounds such as antioxidants [2]. However, after harvest process, the fresh fruits and vegetables are still continuing the metabolic activity including respiration [3] leading to freshness decay which is not good to growers, retailers and consumers. During this past several decades one of the most interesting solution to prevent the postharvest loss is using the modified atmosphere packaging (MAP) [4]. In general, MAP does not require chemicals to preserve the fresh foods but, instead, it will passively adjust the gas compositions inside the package to reduce the metabolic process of the foods. However, the gas composition adjustment will take time to reach the suitable gas composition for the foods [5].

MAP is a technique used for prolonging the shelf-life of fresh produces. In this technique the gas compositions inside the package are changed from the ambient composition at the beginning to another composition [6] as time passes due to the respiration rate of fresh foods or produces inside the packaging and the permeability of the packaging film (see Fig.1, R_{O2}, R_{CO2} are rates of oxygen and carbon dioxide production, $[yO2]_a$, $[yCO2]_a$ are partial pressures of oxygen and carbon dioxide outside the package, $[yO2]_p$, $[yCO2]_p$ are partial pressures of oxygen, carbon dioxide inside the package, respectively). In fact, the gas compositions suitable for storage of different fresh fruits and vegetables are different from one another. For example, broccoli should be stored at 1-2 O_2 vol% and 5-10 CO_2 vol% and strawberry at 5-10 O_2 vol% and 15-20 CO_2 vol% [4]. Ideally, these suitable gas compositions for storage should be reached as fast as possible to extend the shelf-life as long as possible. However, the problem of commercial films are that they have low O_2 and CO_2 permeability that are not suitable for creating the modified atmosphere condition within a reasonable time [7].

In general, fresh produce continually loses water through transpiration [8]. If the WVTR value of the package is low, the packaging headspace will be saturated and the water vapor water will condensed [9]. This condition will cause high humidity inside the packaging, creating condition favorable for microbial growth [10]. In contrast, the package with too high WVTR value causes fresh fruits and vegetables to lose the moisture quickly [10].

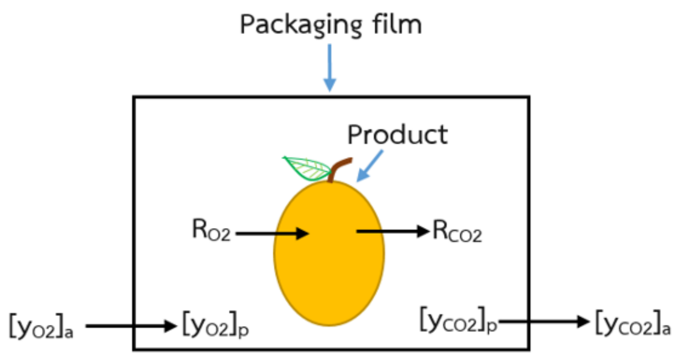

Figure 1. Modified Atmosphere Packaging System

Low density polyethylene (LDPE) is a thermoplastic made from the ethylene monomer. Nowadays, one of the largest markets for LPDE is film for food packaging because LDPE has a good flexibility and easy to process. On the other hand, it has low gas and water vapor permeabilities that are not suitable to use as fresh produce packaging [11]. To improve its permeability, LDPE can be blended with high permeability polymer or perforation technique is used to obtain better gas and water permeabilities [5, 12].

Thermoplastic polyester elastomer (TPEE) is a thermoplastic elastomer which consists of a hard crystalline segment of polybutylene terephthalate and a soft amorphous segment of polyether [13]. General purpose grade TPEE offers good flexibility and toughness. It can easily be processed via injection and extrusion techniques. Many studies have shown that the ether block in copolymer can be a permeable phase due to its high chain mobility [14]. Based on this information TPEE has a potential to be MAP or gas separation membrane [14, 15].

In this research, a new packaging film was developed by blending LDPE with different amount of TPEE with the goal to increase its gas and water vapor permeabilities. The new MAP films were prepared via twin screw extruder with ribbon sheet die. The O_2 and water vapor permeabilities were measured. The differential scanning calorimetry (DSC) was employed to determine the percent crystallinity ($\%X_c$) of the obtained MAP films.

Materials and methods

Materials

LDPE resin trade name Innoplus, grade 2420k, was purchased from PTT Global Chemical, Thailand. TPEE resin, trade name Hytrel, grade G3548 NC010, was purchased from Dupont, USA.

Methods

Blending process

In this research the wt% compositions of LDPE/TPEE were 100/0, 90/10, 80/20, 70/30, 50/50 and 0/100. LDPE resin and TPEE resin were dried in vacuum oven at 80 °C for 3 hr. After drying, the LDPE and TPEE resin were mixed by dry-blend method. Then the mixed resin were fed to twin screw extruder. Finally, the extrudate was cut to small pellet and dried in vacuum oven at 80 °C for 3 hr.

Film preparation

The pellet from blending process was fed to twin screw extruder with ribbon sheet die. The barrel temperature from feed-zone to die-zone were kept constant at 150, 170, 180, 180, 180 and 180 °C. Chill roll temperature was kept constant at 35 °C. The screw speed was 100 rpm. To make sure that film thickness was nearly constant around 40 micron, the pulling speed and feed rate were kept constant at 200 rpm and 35 rpm, respectively.

Oxygen and water vapor transmission rate

Oxygen transmission rate (OTR) of films were measured using the oxygen permeability analyzer (OX-TRAN® Model 2/21 module ST, Mocon, USA) at 23 °C and 0 %RH following ASTM D3985. Oxygen gas at 99.7% purity and mixed gas (Nitrogen gas 98% + Hydrogen gas 2%), purchased from Linde, Thailand, were used as test gas and carrier gas, respectively.

Water vapor transmission rate (WVTR) of films were measured using water vapor permeability analyzer (PERMATRAN-W® Model 398, Mocon, USA) at 25 °C and 50 %RH following ASTM E398. HPLC grade water was added to chamber and nitrogen gas 98% purity was used as carrier gas.

Thermal properties

Thermal properties of films, namely, %Xc and crystallization temperature (T_c), were analyzed using the differential scanning calorimeter (Mettler Toledo DSC1 STAR^e System). The samples were packed in aluminum pan and heated from 25 to 190 °C at a heating rate of 10 °C/min and then cooled down to 25 °C at a cooling rate of 10 °C/min. The measurement was performed in duplicate under nitrogen atmosphere with a nitrogen flow rate of 50 mL/min.

Results and discussion

Results

Oxygen transmission rate (OTR)

Oxygen concentration in the MAP is an important factor in controlling the rate of respiration of fruits and vegetables. To create the low concentration of O_2 inside the package, the OTR of the film should be low to cause oxygen from the outside of the package to penetrate into the package slowly. However, the OTR of the film should not be too low to produce very low O_2 concentration inside the MAP which consequently will lead to the undesirable anaerobic respiration [16]. Figure 2 indicated the increasing of OTR of the blended film when TPEE content was increased. Neat LDPE film (0 wt% TPEE content) showed OTR of 4,187.4±96.1 cc/m^2 day, while neat TPEE showed OTR of 16,505.9±784.5 cc/m^2 day which was about 4 times of that of LDPE. This phenomenon occured due to ether block in TPEE. Generally, the ether block has high chain mobility that allows O_2 to permeate easily [14, 17].

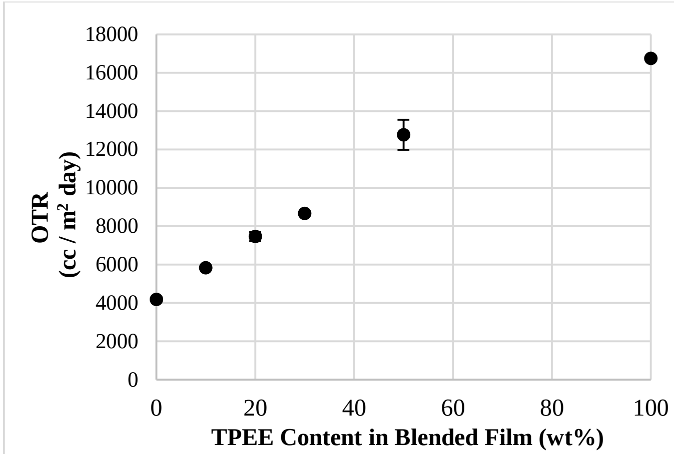

Figure 2. OTR of the MAP Films

Water vapor transmission rate (WVTR)

Humidity inside the packaging is an important factor for keeping the freshness of fruits and vegetables. The package with too high WVTR value causes fresh fruits and vegetables to lose the moisture quickly. On the other hand, if the WVTR value is too low, the condensation of water vapor will occur inside the package [9] which will cause spoilage in fresh produces. Figure 3 revealed that WVTR of MAP films increased with increasing TPEE content. Neat LDPE film (0 wt% TPEE content) showed WVTR of 14.18±0.47 gm/m^2 day, while neat TPEE showed WVTR of 140.79±2.15 gm/m^2 day. Clearly, the WVTR of the neat TPEE was almost 10 times of that the neat LDPE. This implied that the TPEE has a high degree of permeability to polar molecules such as water [18] because ether block in TPEE has high chain mobility that allows water vapor to permeate easily [14, 17].

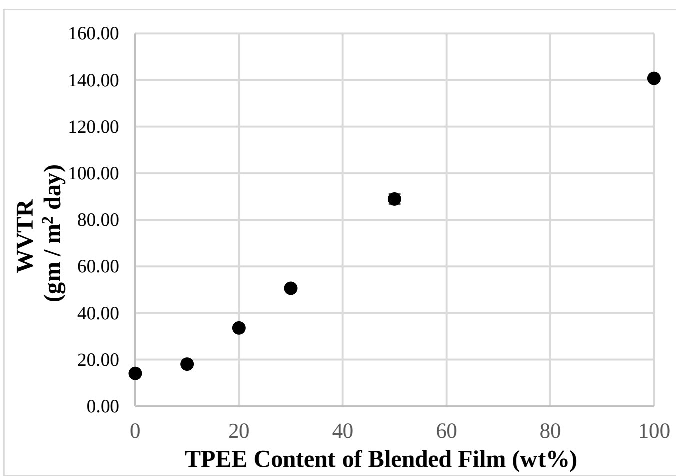

Figure 3. WVTR of the MAP films

Thermal properties

The DSC measurement clearly showed that all MAP films have a crystalline structure. The crystalline temperatures (T_c) were in range of 107.7±0.5 to 111.1±0.5 °C. The T_c results of neat LDPE and neat TPEE were approximately correlated with those obtained by Liu et al. [19] and Chen et al. [20], respectively. In addition, MAP film with TPEE 10 wt% showed the highest %X_c because the presence of dispersed TPEE particles in a LDPE matrix and TPEE particles can act as nucleating agent in the matrix [21].

Table 1. Crystallization temperature (T_c) and percent crystallinity (%X_c) of MAP films

MAP Films (LDPE/TPEE)	T_c (°C)	%X_c
Neat LDPE 100/0	111.1±0.5	23.24±0.32
LDPE/TPEE 90/10	111.0±0.3	25.49±0.63
LDPE/TPEE 80/20	111.0±0.3	24.16±0.65
LDPE/TPEE 70/30	110.9±0.6	22.13±0.49
LDPE/TPEE 50/50	110.5±1.0	15.61±0.63
Neat TPEE 0/100	107.7±0.5	8.56±0.28

Conclusion

In summary, the blending of LDPE and TPEE was successful. The new MAP films were found to possess the better oxygen and water vapor permeabilities than the commercial LDPE films by increasing the contents of TPEE. Moreover, adding small amount of TPEE can also increase %X_c of the MAP films because the presence of dispersed TPEE particles can act as nucleating agent for the crystallization process. Consequently, the new MAP films can be a good candidate in fresh fruits and vegetables packaging application.

References

Journal:

1. Lamuela, R., Rosa, M.M., Alexander, T.R., Anna, E. and Ramón, R., *Fruit and Vegetable Polyphenol Consumption Decreases Blood Pressure.* Emerging Trends in Dietary Components for Preventing and Combating Disease, 2012. **1093**(1093): p. 443-461.
2. Renard, C.M., *Extraction of bioactives from fruit and vegetables: State of the art and perspectives.* LWT, 2018. **93**: p. 390-395.
3. Kader, A.A. *Fruit Maturity, Ripening, and Quality Relationships*. 1999. International Society for Horticultural Science (ISHS), Leuven, Belgium.
4. Kirkland, B.S., Clarke, R. and Paul, D.R., *A versatile membrane system for bulk storage and shipping of produce in a modified atmosphere.* Journal of Membrane Science, 2008. **324**(1): p. 119-127.
5. Xanthopoulos, G., Koronaki, E.D. and Boudouvis, A.G., *Mass transport analysis in perforation-mediated modified atmosphere packaging of strawberries.* Journal of Food Engineering, 2012. **111**(2): p. 326-335.
6. Sandhya, *Modified atmosphere packaging of fresh produce: Current status and future needs.* LWT - Food Science and Technology, 2010. **43**(3): p. 381-392.
7. Belay, Z.A., Caleb, O.J. and Opara, U.L., *Modelling approaches for designing and evaluating the performance of modified atmosphere packaging (MAP) systems for fresh produce: A review.* Food Packaging and Shelf Life, 2016. **10**: p. 1-15.
8. Castellanos, D.A., Herrera, D.R. and Herrera, A.O., *Modelling water vapour transport, transpiration and weight loss in a perforated modified atmosphere packaging for feijoa fruits.* Biosystems Engineering, 2016. **151**: p. 218-230.
9. Fereydoon, M. and Ebnesajjad, S., *5 - Development of High-Barrier Film for Food Packaging*, in *Plastic Films in Food Packaging*. 2013, William Andrew Publishing: Oxford. p. 71-92.
10. Kader, A.A., Zagory, D., Kerbel, E.L. and Wang, C.Y., *Modified atmosphere packaging of fruits and vegetables.* Critical Reviews in Food Science and Nutrition, 1989. **28**(1): p. 1-30.
11. Massey, L.K., *Chapter 36 - Low Density Polyethylene (LDPE)*, in *Permeability Properties of Plastics and Elastomers (Second Edition)*. 2003, William Andrew Publishing: Norwich, NY. p. 219-226.
12. Mahajan, P.V., Oliveira, F.A.R., Montanez, J.C. and Frias, J., *Development of user-friendly software for design of modified atmosphere packaging for fresh and fresh-cut produce.* Innovative Food Science & Emerging Technologies, 2007. **8**(1): p. 84-92.
13. Massey, L.K., *Chapter 72 - Polybutadiene Thermoplastic Elastomer (TPE)*, in *Permeability Properties of Plastics and Elastomers (Second Edition)*. 2003, William Andrew Publishing: Norwich, NY. p. 435-437.
14. Armstrong, S., Freeman, B., Hiltner, A. and Baer, E., *Gas permeability of melt-processed poly(ether block amide) copolymers and the effects of orientation.* Polymer, 2012. **53**(6): p. 1383-1392.
15. John, W.S., *Block polyester-ether gas separation membranes*. 2005: United State.
16. Dumont, M.J., Orsat, V. and Raghavan, V., *7 - Reducing Postharvest Losses A2 - Madramootoo, Chandra*, in *Emerging Technologies for Promoting Food Security*. 2016, Woodhead Publishing: Oxford. p. 135-156.

17. Kim, J.H., Ha, S.Y. and Lee, Y.M., *Gas permeation of poly(amide-6-b-ethylene oxide) copolymer.* Journal of Membrane Science, 2001. **190**(2): p. 179-193.
18. Dupont, *Dupont™ Hytrel® Thermoplastic Polyester Elastomer Design Guide*. 2018, USA.
19. Liu, C., Wang, J., and He, J., *Rheological and thermal properties of m-LLDPE blends with m-HDPE and LDPE.* Polymer, 2002. **43**(13): p. 3811-3818.
20. Chen, J., Lu, Q., Wu, D., Yao, X., Wang, J. and Li, Z., *Nucleation of a Thermoplastic Polyester Elastomer Controlled by Silica Nanoparticles.* Industrial & Engineering Chemistry Research, 2016. **55**(18): p. 5279-5286.
21. Lotti, C., Correa, C.A. and Canevarolo, S.V. *Mechanical and morphological characterization of polypropylene toughened with olefinic elastomer.* Materials Research, 2000. **3**: p. 37-44.