Effects of $CaCO_3$ Content and Stretching Ratio on PE Film Properties

Visanu Tanboonchuy[1]
Somjai Kajorncheappun-ngam[2*]

Abstract

This research studied the effects of variables on the properties of low density polyethylene (LDPE) film. These variables were the portion of calcium carbonate ($CaCO_3$) in PE and the stretching ratio of the PE film forming. The portion of $CaCO_3$ in the range of 0-50 % (by weight) was mixed with PE, then processed to be a thin PE film by a blown film extruder at different stretching ratio (i.e. 100%, 135%, 150% and 170%). Properties of these PE film, such as tensile strength and elongation at failure, water vapor transmission rate (WVTR), oxygen transmission rate (OTR) and fractured surface of the PE film under scanning electron microscopy (SEM), were determined. The results showed that when the portion of $CaCO_3$ was increased it increased both the water vapor transmission rate and oxygen transmission rate, while reduced the tensile strength and elongation at failure. Increasing the stretching ratio of the PE film forming also increased both the water vapor and oxygen transmission rate. For the film containing the same portion of $CaCO_3$, increasing the stretching ratio resulted in the increase in tensile strength. The results of scanning electron microscopy confirmed that the distribution of $CaCO_3$ particles was uniformed. The stretching ratio during film formation affected the pore size around $CaCO_3$ particles, since the area of pore would increase when the stretching ratio increased.

Keywords: Polyethylene, Porous film, Permeable film

[1] *Graduate, Master of Engineering Program in Chemical Engineering, Faculty of Engineering, Khon Kaen University*
[2] *Associate Professor, Chemical Engineering Department, Faculty of Engineering, Khon Kaen University*
**Corresponding author, e-mail: ksomja@kku.ac.th*

Introduction

Since Thailand is one of the major agricultural crop suppliers, its fresh produce have been exported to countries all over the world. However, the exported fresh produce were short-lived, therefore, initially, they were kept at low temperature to preserve their freshness by lowering their metabolic process rate (Cazier, 2001). However, this method also increases the cost for supplier. The Modified Atmosphere Packaging (MAP) technique was thus developed and introduced to prolong shelf-life period of perishable product like meat, fish, fruit and vegetables. In this preservation technique the air surrounding the products in the package is changed to another composition. By this way the shelf-life of fresh products will be prolonged because it slows down the natural deterioration of the product (Sandhya, 2009). Some examples of fresh produce which have been packaged successfully in MAP are mushrooms (Simon et al., 2005), apples (Soliva-Fortuny et al., 2005), tomatoes (Aguaya et al., 2004), potatoes (Beltran et al., 2005), mangos (Beaulieu and Lea, 2003), etc. Additionally, by adding 1-Methycyclopropane in the packaging to absorb generated ethylene also helped prolong freshness in bananas (Jiang, 1999).

Polymer film which are widely used as packaging material in MAP are, for instance, Low Density Polyethylene (LDPE), Polyvinyl Chloride (PVC), Polypropylene (PP), etc. Properties of polymer films such as film ability to O_2, CO_2, water vapor and film strength worth considering in selecting polymer film used in MAP. Since a particular type of fresh product needs a particular packaging property to prolong its shelf-life period. Although many of the films are used in MAP, there is no single film offers all the properties required for a modified atmosphere packagmg. To provide packaging films with a wide range of properties, many researches and experiments in porous film production have been developed. One example is the experiment in producing porous film by mixing high density PE with small particle starch (particle size less than 14.8 micrometer) at different ratios of 2%, 4%, 6%, 8%, and 12% (by weight). Then the starch was washed away from polymer to generate macro pores on the polymer matrix. The research showed that after increasing portion of starch in the mixture, the number of pores would increase accordingly. On the contrary, this would decrease the PE film's tensile strength and elongation (Sa-nguanruksa et al., 2004). The effects of film coating on film's mechanical property were also studied. The film was made of a mixture of PE and zeolite. The film was then coated with stearic acid. It was found that the mechanical properties of the film, e.g. impact resistance and Young Modulus were higher than those without the acid coating (Kim et al., 2006). In addition, mathematical models were developed to forecast the correlations between the portion of calcium carbonate content and water vapor transmission rate in PE film (Hale et al., 2001). According to the research, it was indicated that the water vapor transmission rate increased with the size and quantity of film pores.

After reviewing relevant researches, both domestically and internationally, we found that most of them focused on controlling the condition within the packages. Besides, the film used for those MAPs were mostly produced under conventional processes, which were suitable for fresh produce with low-to-medium respiration rate (although harvested, fresh produce still breathe). On the other hand, if these polymer films were used for fresh produce with high respiration rate, such as broccolis and cabbages, these produce would rot. As a result, the industrial sector was much more interested in the research and development for polymer films with high gas transmission rate (Sandhya, 2009 cited from Lange, 2000). Moreover, there were only a few researches focusing on manufacturing high gas-transmission films, by adding calcium carbonate. This research, therefore, aims to produce such polymer film by emphasizing on variables affecting its mechanical properties, as well as gas transmission rate. Specifically, this research work focused on the film which derived from PE, with calcium carbonate as filler. Two variables, the portion of calcium carbonate ($CaCO_3$) content and the stretching ratio during film formation, were selected to study because these variables would affect the water vapor transmission rate, oxygen transmission rate, as well as mechanical properties of film. Calcium carbonate was chosen in the research due to the fact that they are low cost and they do not interact with polymer. Ultimately, this research would provide information on gas transmission and mechanical properties of PE film under various conditions, thus a mathematical model could be developed accordingly. Simulated results from the models are expected to save entrepreneurs tremendous amount of time and cost on selecting optimal conditions for producing desired film.

Methodology

Raw Materials and Experiment Equipments

Raw materials mainly used in this research were: plastic resin, LDPE (Grade: EL-Lene LD 1902FA), with a melt flow rate (MFR) of 2.00 g/ 10 min from Thai Polyethylene (1993) Co., Ltd. ; and $CaCO_3$ (Grade: Omyacarb 1T), with size smaller than 2 micrometer from Surint Omya Chemicals (Thailand) Co.,Ltd. Equipments used for polymer film forming were: twin screw extruder (Model: DSE 25, L:D =20, Brabender OHG Duisburg Co., Ltd., Germany) and blow film extruder (Model: AH40, AR Product Co., Ltd., Thailand).

Film Forming Process

Weighed plastic resin and $CaCO_3$, with $CaCO_3$ content of 0%, 10%, 25%, and 50% (by weight). Then, load the mixture into the twin screw extruder to blend the material homogeneously. The compound was then heated at 100 degree Celsius for 4 hours to dehumidify. Afterwards, the film was processed to a thin PE film by the blow film extruder. The temperature of the extruder was set up as follow: Feed Zone at 163 degree Celsius; Metering Zone 1 and 2 at 165 degree Celsius; and Die Zone at 170 degree Celsius. During the film forming process, the stretching ratio was adjusted at 4 various ratios, i.e. 100%, 135%, 150%, and 170% for each compounding mixture. The film width and thickness was controlled at 45 cm. and 0.02 mm., respectively.

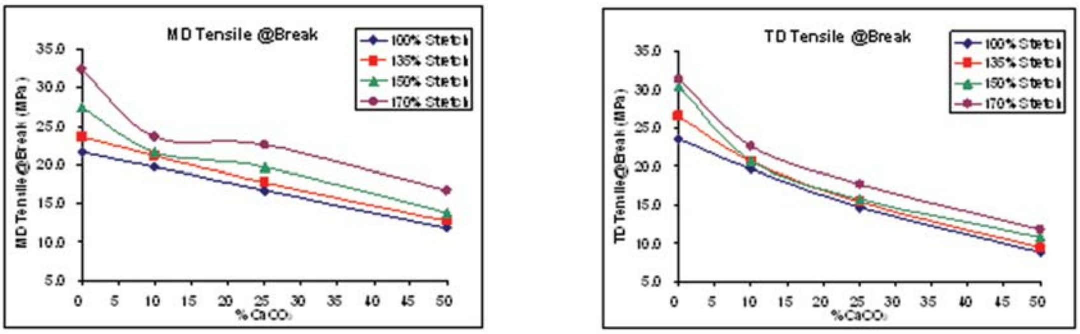
Film Property Test

The finished PE film was tested for its tensile strength and elongation under ASTM D882. Moreover, the water vapor transmission rate (WVTR) and the oxygen transmission rate (OTD) were also determined under ASTM E398 and ASTM D3985, respectively. Finally, the film surface characteristics as well as the distribution of $CaCO_3$ particles on the film were investigated by the Scanning Electron Microscope (SEM).

Results and Discussion

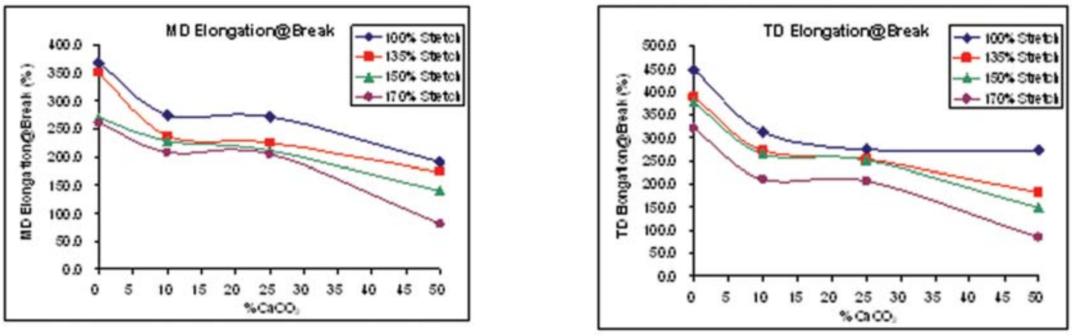
Effects of $CaCO_3$ Content and Stretching Ratio on Tensile Strength and Elongation

Figure 1 and 2 are graphs showing the effects of $CaCO_3$ content and stretching ratio on the film's tensile strength and elongation at break in the Machine Direction (MD) as well as the Transverse Direction (TD). It was shown that the tensile strength and elongation in both MD and TD decreased when the $CaCO_3$ content was increased. This is due to the fact that $CaCO_3$ particles, which are inflexible solid, have infiltrated the polymer matrix, causing the film to be discontinuous or less homogeneous. The micrograph of SEM in Figure 3 confirmed the effect, by showing the film fracture around the area where $CaCO_3$ particles and polymer matrix were discontinuous, thus the film's strength decsreased. Furthermore, when considered at the same amount of $CaCO_3$ containing in the film it was found that tensile strength would vary directly with the stretching ratio. This is because the stretching force enhanced the orientation of the PE molecules to be in the stretching direction (machine direction). As a result, the film strength increased in machine direction. The elongation at break, on the other hand, was decreased (see Figure 2).



(A) (B)

Figure 1. Correlations between $CaCO_3$ content and tensile strength at various stretching ratio during film formation along (A) MD and (B) TD



(A) (B)

Figure 2. Correlations between $CaCO_3$ content and elongation at various stretching ratio during film formation along (A) MD and (B) TD

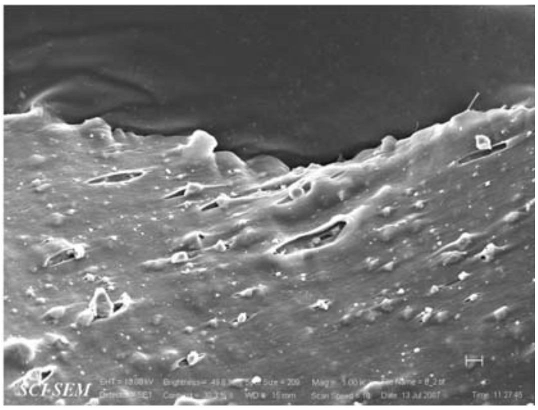
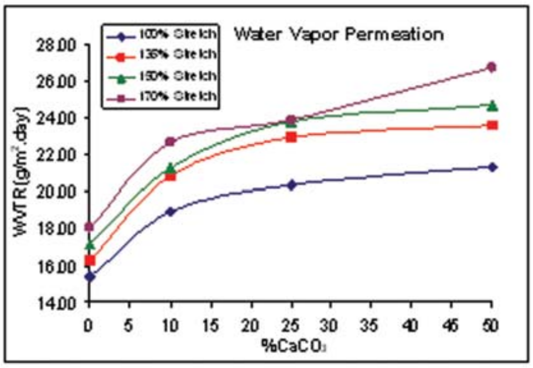


Figure 3. SEM micrograph illustrating the torn film (25% $CaCO_3$ by weight) after tensile strength test (100X magnification)

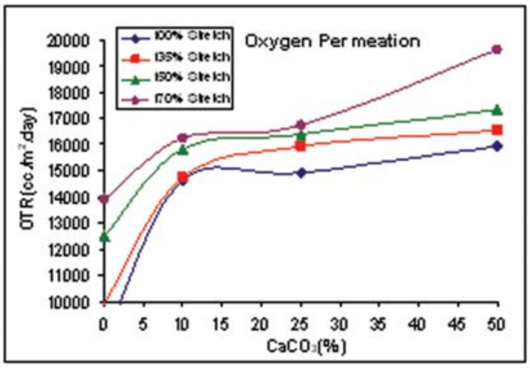
Effects of $CaCO_3$ Content and Stretching Ratio on Water Vapor and Oxygen Transmission Rate

Water vapor transmission rate (WVTR) and oxygen transmission rate (OTR) of polymer film depend on its physical properties, i.e. pore size and number of pores on the film. The pore size on the film varies with these factors: percent content of $CaCO_3$ in the film and stretching ratio during film formation.

Figure 4 is a graph showing that water vapor and oxygen transmission rate increased as $CaCO_3$ content was increased. The reason for this phenomenon was that water vapor and oxygen can pass through pores on the film around the interface between $CaCO_3$ particles and PE matrix, therefore, the more $CaCO_3$ content put into the film, the more pores there were for water vapor and oxygen to diffuse through. In addition, the stretching ratio during film formation also enlarges those pores allowing even more water vapor and oxygen diffuse through the film. This can be confirmed by the evidence showing in Figure 5. Figure.5 illustrates the phenomenon from SEM micrograph, showing larger pore between $CaCO_3$ particles and PE matrix, when stretching ratio was increased.

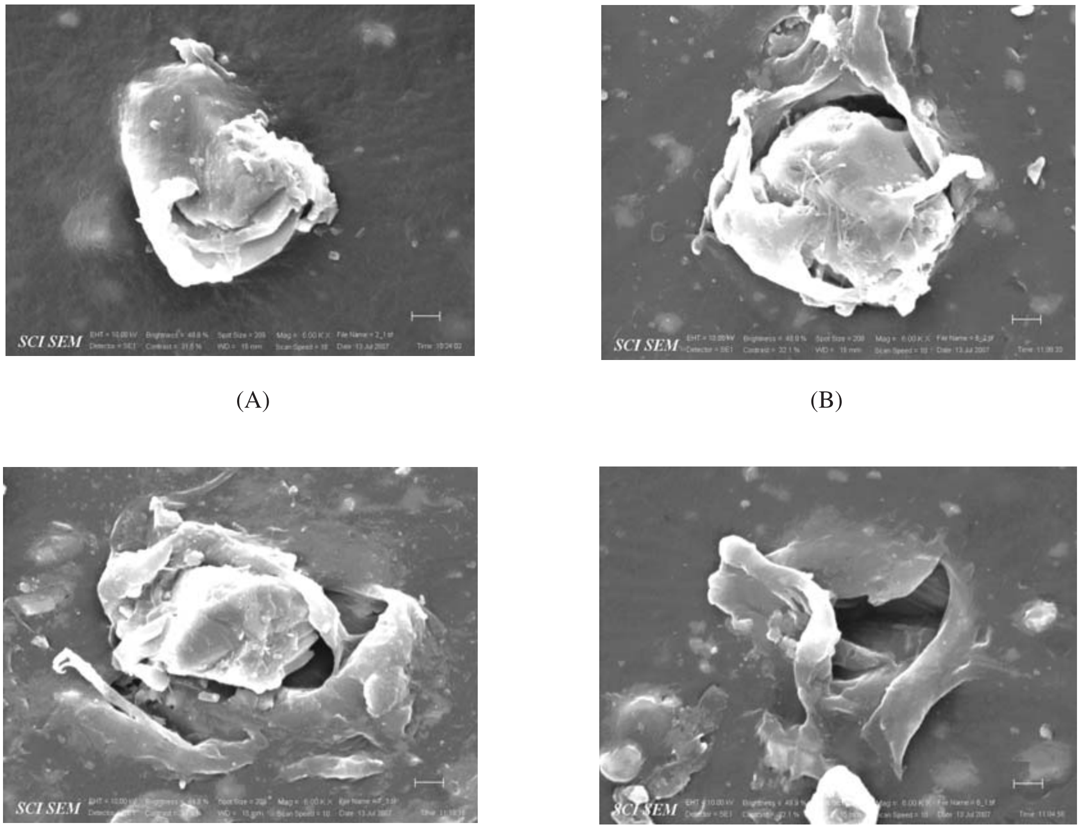


(A)



(B)

Figure 4. Correlations between $CaCO_3$ content and gas transmission rate at various stretching ratio during film formation (A) water vapor transmission rate and (B) oxygen transmission rate



(A) (B)

(C) (D)

Figure 5. SEM micrograph illustrating interfacial area between $CaCO_3$ particles and PE film with 25% $CaCO_3$ content at various stretching ratio (A) 100% (B) 135% (C) 150% and (D) 170% (6000X magnification)

Mathematical Model

The 2 independent variables considered in the research are $CaCO_3$ content and stretching ratio during film formation. Figure1, 2 and 4 show how these 2 variables affected PE film's mechanical properties, water vapor and oxygen transmission rates respectively. Experimental data plotted in these 3 Figures were used to develop mathematical models in second-degree polynomial equations (Meyer and Montgomery, 1995), as shown in Eq.1

$$Y = a + b(X_1) + c(X_2) + d(X_1*X_2) + e(X_1^2) + f(X_2^2) \quad (1)$$

Where:

Y	:	Property of film
X_1	:	Stretching ratio during film formation (%)
X_2	:	$CaCO_3$ content in film (%)
a, b, c, d, e, f	:	Constant

In Microsoft Excel, function "Solver" was used to solve for constants a, b, c, d, e and f in Eq.1. Afterwards, the mathematical model was validated by plotting correlations between actual results from the experiment (Y-Axis) and estimated results from the mathematical model (X-Axis). The Correlation Coefficient (R^2) was also validated. After the input of those predetermined value of a, b, c, d, e, and f in Eq.1, equations for predicting PE film's properties were developed, as shown in Eq.2 - 7.

$$\text{MD Tensile} = 33.76-0.255X_1-0.1834X_2-0.0012X_1X_2+0.0014X_1^2+0.0021X_2^2 \quad (2)$$

$$\text{TD Tensile} = 24.73-0.051X_1-0.4869X_2-0.0011X_1X_2+0.0005X_1^2+0.0058X_2^2 \quad (3)$$

$$\text{MD Elongation} = 342.78+0.7845X_1-3.8991X_2-0.0006X_1X_2-0.076X_1^2+0.0195X_2^2 \quad (4)$$

$$\text{TD Elongation} = 354.01-1.6439X_1-4.9354X_2-0.0189X_1X_2-0.0108X_1^2+0.0747X_2^2 \quad (5)$$

$$\text{WVTR} = 10.56+0.0543X_1+0.2597X_2+0.0007X_1X_2-0.0001X_1^2-0.0043X_2^2 \quad (6)$$

$$\text{OTR} = 13161-80.9733X_1+329.0988X_2-0.3098X_1X_2+0.4941X_1^2-3.5382X_2^2 \quad (7)$$

The mathematical models were validated by determining R^2 values, which, in this research, were 95.24%, 97.77%, 89.55%, 91.14%, 96.86%, and 86.88%, for MD tensile, TD tensile, MD elongation, TD elongation, water vapor transmission rate, and oxygen transmission rate, respectively. The R^2 obtained in the research confirmed that results estimated by the mathematical models for each film property were within the acceptable accuracy range.

These models would be useful for predicting PE film properties, such as tensile strength, oxygen and water vapor transmission rate under other various process conditions. For instance, they can predict PE film property at any other different portion of $CaCO_3$ content containing in film (only 4 different portions of $CaCO_3$ content were used in this research: 0%, 10%, 25%, and 50%). Similarly, the desired film property could easily be predicted by the mathematical model at any other stretching ratio without having to set up another experiment. Additionally, we may wish to determine the tensile strength, elongation, water vapor and oxygen transmission rate for PE film, specifically, with 35% $CaCO_3$ content and 115% stretching ratio. Eq.2 - 7 could be used to predict the film properties without having to make the actual film for experiments. This would greatly reduce time and cost for entrepreneurs in the film manufacturing process.

Conclusion

From the experiment, it was found that both portion of $CaCO_3$ content in the film and the stretching ratio during film formation, affected the film's tensile strength, elongation, water vapor and oxygen transmission rate. Specifically, the more $CaCO_3$ content used, the more water vapor and oxygen transmission rate would be. On the contrary, it reduced tensile strength and elongation at break of the PE film. Increasing stretching ratio enhanced both water vapor and oxygen transmission rate. As for the film with the same $CaCO_3$ content, the stretching ratio helped the PE molecules to be oriented in the stretching direction, thus giving it more tensile strength in the machine direction.

Acknowledgement

This research was sponsored by Khon Kaen University in the General Sponsor Category for the budget year of 2009. We would like to thank Thai Polyethylene (1993) Co., Ltd. and Surint Omya

Chemicals (Thailand) Co.,Ltd. for providing raw materials for the experiment, as well as the Polymer Engineering Department, Suranaree University of Technology for providing the experiment equipments.

References

Aguayo, E., Escalona, V. and Artes, F. 2004. Quality of fresh-cut tomato as affected by type of cut, packaging and storage time. **European Food Research and Technology** 219(5): 492-499.

Beaulieu, J.C. and Lea, J.M. 2003. Volatile and quality changes in fresh-cut mangoes prepared from firm-ripe and soft-ripe fruit stored in clamshell containers and passive MAP. **Postharvest Biology and Technology** 30(1): 15-28.

Beltran, D., Selma, M.V., Tudela, J.A. and Gil, M.I. 2005. Effect of different sanitizers on microbial and sensory quality of fresh-cut potato strips stored under modified atmosphere or vacuum packaging. **Postharvest Biology and Technology** 37(1): 37-46.

Cazier, J.B. 2001. **Mathematical modeling of gas exchanges in film-wrapped cucumber.** [Docteral Thesis in Crop Science] Sweden: Department of Crop Science, University of Agricultural Sciences.

Hale, W.R., Dohrer, K.K., Tant M.R. and Sand, I.D. 2001. A diffusion model for water vapor transmission through micro-porous polyethylene/$CaCO_3$ films. **Physicochemical and Engineering Aspects** 187-188: 483-491.

Jiang, Y., Joyce, C.D. and Macnish, J.A. 1999. Extension of shelf life of banana fruit by 1-Methylcyclopropane in combination with polyethylene bag. **Postharvest Biology and Technology** 16(2): 187-193.

Kim, H., Biswas, J. and Choe, S. 2006. Effect of stearic acid coating on zeolite in LDPE, LLDPE, and HDPE composite. **Polymer** 47: 3984-3992.

Lange, D.L. 2000. New film technologies for horticultural products. **Horticultural Technology** 10: 487-495.

Meyer, R.H. and Montgomery, D.C. 1995. **Response surface methodology: Process and product optimization using designed experiment.** Hoboken, New Jersey:John Wiley & Sons Inc.

Sa-nguanruksa, J., Rujiravanit, R., Supaphol, P. and Tokura, S. 2004. Porous polyethylene membranes by template-leaching technique: preparation and characterization. **Polymer Testing** 23: 91-99.

Sandhya. 2009. Modified atmosphere packaging of fresh produce: Current status and future needs. **LWT-Food Science and Technology** article in press.

Simon, A., Gonzalez-Fandos, E. and Tobar, V. 2005. The sensory and microbiological quality of fresh sliced mushroom (*Agaricus bisporus* L.) packaged in modified atmospheres. **International Journal of food Science and Technology** 40(9): 943-952.

Soliva-Fortuny, R.C., Ricart-Coll, M. and Martin-Belloso, O. 2005. Sensory quality and internal atmosphere of fresh-cut Golden Delicious apples. **International Journal of food Science and Technology** 40(4): 369-379.