Effect of essential oil on properties of PBAT/PBS for bio-packaging films

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This research aimed to study the effect of essential oil on the mechanical and barrier properties of bio-packaging films from a polymer blend between polybutylene adipate-co-terephthalate and polybutylene succinate (PBAT/PBS) using the β-cyclodextrin (βCD) as controlled release for sweet basil essential oil (ES). PBAT grafted with maleic anhydride (PBAT-g-MA) is used as compatibilizer between polymer matrix and β-cyclodextrin. The MA grating content is found to be 2.47% w/w. The preparation of PBAT/PBS blend films with two weight ratios includes 80/20 and 60/40 with varied βCD-ES contents of 0, 0.25, 0.50, 0.75 and 1.00 phr. Tensile strength and elongation at break were increased when β-cyclodextrin with essential oil decreasing. Considering the ratio of PBAT/PBS, the mechanical properties i.e., tensile strength, Young’s modulus and elongation at break of PBAT/PBS film at weight ratio of 80/20 incorporated with βCD-ES were higher than the ones at weight ratio of 60/40. For barrier properties, water vapor and oxygen permeability of PBAT/PBS films incorporated with lower essential oils content would be decreased. For antimicrobial test, PBAT/PBS with βCD-ES film packaging could effectively inhibit the mold growth on tomatoes after 40 days.

1. Introduction

Petroleum-based plastic packaging has caused environmental concerns e.g. wastes, deteriorating soil and water quality. They are also harmful to natural lives either inland or in the water. Therefore, people nowadays are very keen towards the use of biodegradable plastics, especially for packaging. Our group has chosen biodegradable polymers, namely polybutylene adipate-co-terephthalate (PBAT) and polybutylene succinate (PBS), which are environmentally friendly packaging films. More importantly, their mechanical properties are so practically useful and similar to those of low density polyethylene. [1]

Fruits and vegetables are typically consumed when fresh or as the raw materials for food processing. They are raw materials that easily spoil because of high amount of water and protein content. Additionally, meat products possess a great amount of nutrients that are suitable for the bacterial growth. The microorganisms which spoil the agricultural products and change their texture and smell including the taste of meats are, for instance, Staphylococcus and Escherichia coli [2]. In order to withstand these microorganisms, researchers have selected the sweet basil essential oil as an antibacterial agent due to its richness in natural substances such as d-linalool and eugenol which effectively inhibit bacteria [3]. However, the essential oil could easily be evaporated during the film-forming process. Therefore, β-Cyclodextrin is used as absorber because of its structure with seven glucose subunits creating a cone-shaped cup. The essential oil substances could then access into the cup and interact by intermolecular bonding force. However, β-Cyclodextrin is the polar molecule that could not be compatible with polymer blends. Therefore, it is necessary to use polybutylene adipate-co-terephthalate grafted maleic anhydride (PBAT-g-MA) as a compatibilizer. The objectives of this research are to study the effect of sweet basil essential oil on mechanical and barrier properties of packaging films from polymer blend between PBAT and PBS.
2. Experimental

2.1 Materials
PBAT and PBA were provided from the BASF company (Germany) and PTT MCC Biochem Company (Thailand), respectively. β-Cyclodextrin used as an essential oil absorber, Dicumyl peroxide purity 98% and Maleic anhydride were purchased from Sigma-Aldrich Company (USA). Sweet basil oil was obtained from Chemipan company.

2.2 Film preparation
PBAT-g-MA preparation: maleic anhydride 2 phr was dissolved in acetone 15 ml and dicumyl peroxide 0.1 phr was dissolved in acetone 5 ml. Then, dicumyl peroxide solution was dropped onto PBAT, after that maleic anhydride solution was dropped onto PBAT and mixed together, then melt blended in twin-screw extruder at temperature of 140-180 °C, screw speed of 50 rpm. Extruded was cooled using air at room temperature and then cut into the pellet.

Film preparation: PBAT, PBS and PBAT-g-MA are dried in the oven at 50-60 °C for 24 hr. Then PBAT, PBS, PBAT-g-MA and sweet basil essential oil absorbed into β-Cyclodextrin are compounded by twin-screw extruder at the temperature of 130-165 °C from the hopper to die head using a screw speed of 50 rpm and cooling by air and cutting into pellet. Next, plastic pellets were molded into a thin film by cast film extruder using the temperature at the hopper to die head at 140-160 °C with a screw speed of 50 rpm to control the thickness in the range of 80-100 μm.

2.3 Characterization
Tensile strength, elongation at break and Young’s modulus were tested by using a Universal Testing Machine (Model 5969 Instron Engineering Corporation, USA) according to ASTM D882 standard. The films were cut into rectangular strips (1×4 inch²), and the initial grip separation was set at 2 inches with a tensile rate of 500 mm/min. The surface morphology of the blend films was characterized by using a scanning electron microscope (Model Tabletop Microscope TM3030, Hitachi High-Technologies Ltd., Japan). The fractured films were mounted on a metal stub and then sputtered coated with gold. Samples were observed with an operating voltage of 15 KV. The extracted solution was evaluated for the concentration of essential oil extracts using UV- VIS Spectroscopy (Model UV-1800, Shimadzu Ltd.) technique at wavelengths in the range of 200 to 700 nm, by comparing the absorbance of the extracted solution with the standard curve obtained from the preparation of the extract of the essential oil extracts of basil with a known concentration to determinate of the remaining concentration of essential oil extracts in the blend film. For barrier properties, oxygen permeability was analyzed by a GDP-C Gas Permeability Tester conducted according to ASTM D3985 standard. Samples were subjected to control condition to have less than 1 %RH at 23 °C and gas flow rate of 100 cm³/min. For water vapor transmission rate (WVTR) test, silica gel was packed in a test bottle approximate 4/5 of the bottle and the film is sealed with paraffin films and controlled humidity was 75 ± 5 %RH at room temperature. The test bottles were measured for their weight (Wt) that changed at period of times (ti) and compared with initial weight (Wo). The vapor permeation rates were calculated as shown in equation 1 and 2 where A is film area and l is film thickness.

\[
\text{WVTR}_{\text{raw}} \left( \frac{g}{m^2 \cdot \text{day}} \right) = \frac{W_t - W_0}{A t_i} \quad (1)
\]

\[
\text{WVTR}_{\text{normalised}} \left( \frac{g \cdot \text{mil}}{m^2 \cdot \text{day}} \right) = \text{WVTR}_{\text{raw}} \times l \times \frac{1 \text{mil}}{25 \mu m} \quad (2)
\]

For antimicrobial test, the films were sealed tightly on all 3 sides to create plastics bags with the size of 6x7 cm². Tomatoes were packed into the plastic bags, sealed the remaining side tightly and kept in a refrigerator at 10 °C.
3. Results and discussion

3.1 Mechanical Properties

The results of mechanical properties of PBAT/PBS blend films are shown in Figure 1. The mechanical properties of PBAT/PBS are better than those of neat PBAT. This result illustrates the compatibility between PBAT and PBS caused by a transesterification reaction [4]. Furthermore, the increment of PBS content in PBAT/PBS blend films resulted in the increase of Young’s modulus due to strong chains of PBS as seen in Figure 1(b). However, the addition of essential oil trapped into β-cyclodextrin (βCD-ES) lead to a significant decrease in tensile strength (Figure 1d) due to the interruption of the CH chain aggregations from β-cyclodextrin. Thus, it makes the chain displacement during stretching easier, and lead to the discontinuities induced in the polymer matrix by oil droplets [3,5]. Moreover, the βCD-ES acted as a filler for the polymer matrix. The incorporation of βCD-ES into the PBAT/PBS blend films resulted in a strong reaction between fillers and polymer matrix [6], which decreased elongation at the break by the motion restriction of the polymer matrix.

![Figure 1. Effect of weight ratio of PBAT/PBS on of sweet basil essential oil on (a) Tensile strength, (b) Young’s modulus, (c) Elongation at break and effect of sweet basil essential oil on (d) Tensile strength, (e) Young’s modulus and (f) Elongation at break of PBAT/PBS films](image)

![Figure 2. SEM micrographs of PBAT80/PBS20 blend films with βCD-ES (a) 0 phr, (b) 0.25 phr, (c) 0.75 phr, (d) 1.00 phr and PBAT60/PBS40 blend films with βCD-ES (e) 0.75 phr and (f) 1.00 phr](image)

As per Figure 2, it could be seen that PBAT/PBS polymer film possesses relatively smooth surface. Once βCD-ES was added, the surface of the film showed a discrete phase. This could be attributed to the essential oils hindered the consolidation of the main chain, leading to the discontinuous matrix.
Additionally, larger amount of aggregation of βCD-ES was formed which could act as filler in the polymer matrix as shown in Figure 2b-2f.

3.2 The remaining concentration of sweet basil essential oil in films after film forming process
The measurement of the remaining concentration of the ES was performed using UV-VIS Spectroscopy technique at wavelengths in the range of 200 to 700 nm. The peak intensities of the linalool group of sweet basil essential oil at 375 nm were calculated for the concentrations as shown in Figure 3. The concentrations of sweet basil essential oil in the films after the molding process are also illustrated during the first two days with elevated reduced evaporation rate. PBAT/PBS films with the increasing content of βCD-ES at 0.5, 0.75 and 1.00 phr show the decreased evaporation rates when compared on second day are 39%, 38%, and 35% respectively. PBAT/PBS film with βCD-ES 0.50 phr possesses a relatively lower concentration of sweet basil essential oil than the film with more amount of βCD–ES (0.75 and 1.00 phr). Sweet basil essential oil can be absorbed in β-cyclodextrin because the –OH groups of Linalaool and the -OCH₃ groups of Eugenol, a compound within sweet basil essential oils, interact with the -OH group of β-cyclodextrin. And the hydrophobic parts of sweet basil essential oil will enter the inner cyclic oligasaccharide of β-cyclodextrin as seen in Figure 3(b). Sweet basil essential oil stored in a circle of β-cyclodextrin will cause the decreased evaporation rate of the concentration of sweet basil essential oil to slowly take place.

3.3 Water vapor transmission rate (WVTR)

![Figure 3](image3.png) (a) The remaining concentration of essential oil in PBAT/PBS blend films with various β-ES contents and (b) the structural interaction of β-cyclodextrin with the main compound in sweet basil essential oil

![Figure 4](image4.png) Water vapor transmission rate of PBAT/PBS films (a) without and (b) with βCD-ES
Figure 4 shows the WVTR of PBAT, PBS and PBAT/PBS blended films with β-cyclodextrin and essential oil in different ratios. As shown in Fig. 4(a), the water vapor permeability rate of PBAT/PBS film is between the water vapor permeability rate of PBAT film and PBS film. The water vapor permeability rate decreased with increasing the PBS content because the PBS chain possesses relatively high hardness. Hardness obstructs the transmission of water vapor within polymer matrix. The addition of β-cyclodextrin with essential oil (Fig. 4(b)) showed that the water vapor permeability rate of PBAT/PBS blended films was increased as the amount of βCD-ES was increased. βCD-ES could reduce attractive interaction between polymer chains leading to the ease of chain movements. Moreover, the βCD-ES could also increase free volume and thus water vapor could easily pass through the film. [7]

3.4 Oxygen Permeability
Figure 5(a) shows the oxygen permeability of PBAT/PBS films at the various PBAT and PBS ratio. It is shown that the polymer blends between PBAT and PBS have lower oxygen permeability rate (OP) than neat PBAT. However, polymer blends possessed higher OP than the one with neat PBS. Therefore, PBAT/PBS film with higher PBS content (PBAT/PBS ratio of 60/40) has lower OP than the one with 80/20. Regarding the effect of essential oil (Fig. 5(b)), PBAT/PBS films with higher essential oil content have higher oxygen permeability. As the essential oil acts as a plasticizer, the structure of the polymer increases free volume. The polymer chains are easy to move, which corresponds to the mechanical properties. When the essential oil is added, the film tends to reduce its Young’s modulus, which allowed the oxygen to pass through the polymer film easily [7, 8].

![Figure 5](image)

**Figure 5.** Oxygen permeability rate of PBAT/PBS films (a) without βCD-ES and (b) with βCD-ES

3.5 Antimicrobial
Figure 6 shows the physical appearances of tomatoes after storing in the packaging films. After keeping the tomatoes in the packaging films for 7 days, there were some water vapors in the packaging films due to the respiration of tomatoes. When the tomatoes were preserved in the film for 35 days, the packaged tomatoes without essential oils in the film displayed in turbid yellow on the tomatoes skin for PBAT/PBS ratio of 80/20 and turned to be dry and dark skin for PBAT/PBS ratio of 60/40. After being kept for 40 and 45 days, tomatoes packed in the films without essential oils showed more spoilage with molds occurred. In regards to the effects of essential oil, tomatoes contained in the film containing 0.25 phr of essential oil had turbid water and molds on the tomatoes after 40 days. While the product packed in the film containing more essential oil of 0.75 and 1.00 phr did not deteriorate after 45 days.
4. Conclusions
From this research, sweet basil essential oil was chosen to study the mechanical and barrier properties of PBAT/PBS bio-packaging films. Using β-cyclodextrin as an absorber of essential oil was to control the oil release during compounding and film forming process. In addition, PBAT-g-MA was used as the compatibilizer. PBAT, PBS, PBAT-g-MA and β-cyclodextrin with sweet basil oil were compounded by twin screw extruder. Films were produced by cast film extruder. The addition of β-cyclodextrin and essential oil had an effect on the tensile strength at break, elongation at break and Young’s modulus of PBAT/PBS blend films. In addition, PBAT/PBS blend films with higher concentration of essential oils remained more amounts of essential oils in the films than PBAT/PBS blend films of lower concentration of essential oil. The higher amount of PB in PBAT/PBS blend films could improve the tensile strength and Young’s modulus of PBAT/PBS blend films. From SEM results, PBAT/PBS blend film surface was relatively smooth but films with βCD-ES showed the discontinuous phase on the film surface. Moreover, PBAT/PBS blend films possessed the higher tensile strength than the neat polymer. The water vapor and oxygen permeability of PBAT/PBS films are increased in accordance with the amount of essential oils added. And lastly, the PBAT/PBS blend films with sweet basil essential oil could effectively inhibit the mold growth in order to avoid the spoilage for at least 30 days.

Figure 6. Physical appearances of tomatoes after storing for 7, 30, 35, 40 and 45 days in PBAT/PBS blend film at the ratio of (a) 80/20 and (b) 60/40 with βCD-ES content of 0, 0.25, 0.5, 0.75 and 1.00 phr.
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