Effect of zeolite types on properties of polybutylene succinate/polylactic acid films

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Abstract. In the current study, the effect of modified zeolite using (3-aminopropyl) triethoxysilane in polybutylene succinate (PBS) and polylactic acid (PLA) blend was investigated. Two types of modified zeolite i.e., zeolite 5A and 13X at 3 wt% of polymer blend between PBS and PLA were mixed together in twin-screw extruder and thin-films were produced by cast-film extruder. The thickness of each film is between 50 – 70 micron. Mechanical properties, thermal properties, morphological properties and permeability of oxygen, carbon dioxide as well as water vapour were investigated. Adding of zeolite 5A into PBS/PLA blend was found to increase more tensile strength and Young’s modulus with the comparison to zeolite 13X whereas the zeolite 13X and 5A had increased the percentage of elongation at break more than PBS/PLA blend. The zeolite 5A and 13X tended to increase the thermal stability of the composite films. Gas permeation results showed that PBS/PLA with zeolite 5A allowed the permeation of carbon dioxide and oxygen more than 13X in composite films. Moreover, water vapour transmission rate of PBS/PLA with zeolite 5A was higher than the one with zeolite 13X.

1. Introduction
Currently, Thailand has produced and exported agricultural products, such as fruits, with the export value up to 6,419,506,381 baht in 2018 [1] and tends to increase in each year. Due to the landscape and climate of Thailand are suitable for growing tropical fruits, the quality of Thai fruits is good. Therefore, it has a high demand by the international market. However, post-harvest handling is still not good in quality causing the fruit ripens before reaching the international market. There are many technologies in producing packaging that can delay fruit ripening such as active packaging or smart packaging [2].

Due to the population of the world is growing, the world has realized the limit of natural resources. Thus, humans develop plastic that will be used to replace natural resources, but the lifespan of common plastics put impact on the environment is too long, causing plastic waste. Biodegradable plastics are used to conserve the environment. Therefore, the researcher is interested in polybutylene succinate (PBS) and polylactic acid (PLA). The properties of PBS are high flexibility, similarpolyethylene (PE), but the disadvantage of PBS is the lack of transparency. So, PLA is mixed together with PBS because PLA has transparency, good mechanical properties, and good thermal stability [3]. The PBS/PLA blend film also has many desirable properties such as high flexibility.
As mention previously, PBS/ PLA blend has a low ability to absorb ethylene and low permeability of carbon dioxide and oxygen gas. So the researcher is interested in improving its properties by adding zeolite, which has a porous structure and large cavity [4]. Each type of zeolite has a different ability to selective passing through of gases. The type of zeolite that can be selected passing through of carbon dioxide and oxygen must have the pore size that is larger than the molecular size of that gas type. For example, zeolite type that can be selected passing through by carbon dioxide zeolite type 5A and 13X (pore size is about five and eight angstrom respectively) [4] because the zeolite has a pore size larger than the molecular size of carbon dioxide, which is 3.3 angstrom.

This research has aimed to develop food packaging film by adding zeolite and studies the effect of zeolite types (5A and 13X) on physical, mechanical, thermal and morphological properties. Moreover, the permeability of oxygen, carbon dioxide, water vapour of PBS/ PLA film was investigated.

2. Experimental
The formulas of prepared film compounds are PBS/ PLA/Z5A and PBS/ PLA/Z13X. (Z5A and Z13X means zeolite 5A and 13X respectively). The ratio of PBS to PLA is 60:40. Each zeolite was modified by using (3-aminopropyl)triethoxysilane in 2wt% of zeolite. A commercial grade PBS (FZ91PM, MFR 5 g/10min, density 1.26 g/cm³) was produced from PTT MCC Biochem Co. Ltd. (Thailand). PLA (4043D, MFR 6 g/10min) was produced form NatureWork LLC Co. Ltd. (Thailand). Zeolite 5A, 13X and (3-aminopropyl)triethoxysilane were purchased from Sigma Aldrich Co. (Singapore). PBS, PLA and modified zeolite were blended together in twin-screw extruder at 165-180°C. Thin-films were produced by cast-film extruder at 155-175°C.

All 20 samples were prepared to test the mechanical properties. The percentage of elongation at break, tensile strength and Young’s modulus of the films were measured according to ASTM D882 using Universal Testing Machine (5956; Instron Corp.). Thermal properties of the films was performed using Thermal Gravimetric Analyzer (TGA/DSC1, Mettler Toledo) under a nitrogen atmosphere. The water vapour transmission rate was determined using the Cup Method (ASTM E96). The permeability of carbon dioxide and oxygen were measured according to ASTM D3985 using Gas Permeability Tester (GDP-C, Bruggerfeinmechanik). The cross section of films was observed through a scanning electron microscopy (SEM). The films were immersed in liquid nitrogen after which they were broken. The films were sputtered coated with Pd/Au.

3. Results and discussion
As shown in Figs. 1a and 1b, adding zeolite 5A into PBS/ PLA blend leads to increase tensile strength and Young’s modulus more than zeolite 13X. The increase in tensile strength is a result of zeolite 5A allowing the PLA phase to be more compatible with PBS, as can be seen in Figs. 2b and 2c. In terms of Young’s modulus, Young’s modulus was increased by adding zeolite because zeolite is an inorganic compound consisting of alumina and silica that binds to a strong structure. Zeolite will reduce the mobility of the polymer chains, causing the polymer film to become more stiffness [5]. The zeolite 5A has a cubic shape and has a lower polarity when compared to the zeolite 13X[4]. The high polarity causes the zeolite to interact with each other more than zeolite interacts with the polymer. Therefore, the zeolite 13X is more easily agglomeration than zeolite 5A, resulting in the unevenly spreading of zeolite 13X in the polymer phase compared to zeolite 5A (as in Figs. 2b and 2c). PBS/ PLA film with adding zeolite 13X had a lower Young’s modulus than the PBS/ PLA film adding with zeolite 5A. Meanwhile adding zeolite 13X and 5A had increased the percentage of elongation at break more than PBS/ PLA blend in Figs 1c. The increasing in elongation at break is expected to be due to the addition of zeolite into PBS/ PLA blend, making PLA more compatible with PBS. As a result, the PLA chain does not interfere with the PBS chain. Moreover, some parts of (3-aminopropyl)triethoxysilane may be reacted with water [6]. Silanol groups that are formed by the hydrolysis reaction can coupling to form siloxane, which is flexible [7].
Figure 1. Mechanical properties of PBS/PLA and PBS/PLA/zeolite (5A and 13X). (a) Tensile strength (b) Young’s modulus and (c) Elongation at break

Figure 2. SEM micrograph of surface films (a) PBS/PLA (b) PBS/PLA/Z5A and (c) PBS/PLA/Z13X (the red circle is PLA phase in PBS and the yellow circle is zeolite in PBS/PLA blend)

From the analysis using the TGA technique, the thermal degradation behaviour of the composite and the blend films are shown in Figs.3. It is found that all films have two stages of degradation. The initial degradation temperature of the composite film is close to the degradation temperature of PLA. The second degradation temperature is close to the degradation temperature of PBS. The degradation of PLA and PBS are about 350 and 395 degree Celsius, respectively. However, considering the onset temperature, it is found that adding both of types of zeolites (5A and 13X) will increase the onset temperature. The results indicated that zeolite (5A and 13X) increase thermal stability.

Figure 3. TGA thermogram of PBS/PLA From Figs.4a, 4b, it shows that adding zeolites reduce the permeation of carbon dioxide and oxygen because it increases path way for gas movement. Moreover, the zeolite structure is also porous, allowing the zeolite to absorb oxygen and carbon dioxide that are smaller than the zeolite’s pores. Therefore, oxygen and carbon dioxide slowly move out of the films [8]. When considering the type of zeolite, PBS/PLA with zeolite 5A can allow the permeation of
oxygen and carbon dioxide faster than zeolite 13X. This is due to the zeolite 13X has a pore size larger than that of zeolite 5A, carbon dioxide and oxygen can be absorbed in the pores more.

The water vapour transmission rate of PBS/PLA/zeolite is higher than PBS/PLA because zeolites are highly polar compounds. It consists of silica and alumina and can allow water molecules to penetrate into it. Moreover, adding zeolite 5A makes the water vapour transmission rate more than zeolite 13X. Due to zeolite 13X has a larger pore size than that of zeolite 5A, its surface area can absorb more water molecules. Therefore, water molecules can take longer time to spread through the film with zeolite 13X more than the film with zeolite 5A [9].

![Figure 4](image_url)

**Figure 4.** The permeation of PBS/PLA and PBS/PLA/zeolite (5A and 13X) (a) carbon dioxide (b) oxygen and (c) water vapour

4. **Conclusions**

In this research, the effect of zeolite on PBS/PLA properties was investigated. Adding zeolite 5A in PBS/PLA tended to increase the tensile strength, Young’s modulus more than zeolite 13X because zeolite 5A is more evenly distributed and made PLA compatible with PBS better than zeolite 13X. From the TGA, PBS/PLA/zeolite (5A and 13X) make higher thermal stability. Moreover, PBS/PLA with zeolite 13X can absorb carbon dioxide and oxygen more than zeolite 5A whereas PBS/PLA with zeolite 5A allowed the water vapour transmission rate more than zeolite 13X due to the larger pore size of zeolite 13X.

5. **References**

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