Thermal and barrier properties of poly(butylene adipate-co-terephthalate) incorporated with zeolite doped potassium ion for packaging film

P Threepopnatkul1,*, K Wongsuton1, C Jaiaue1, N Rakkietwinai1, and C Kulsetthanchalee2
1Department of Materials Science and Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University, Nakhon Pathom 73000, Thailand.
2Event and Exhibition Design Department, Suan Dusit University, Bangkok 10300, Thailand.
*Corresponding author: poonsubt@yahoo.com

Abstract. In this research, the works were focused on development of film packaging of poly(butylene adipate-co-terephthalate) (PBAT) incorporated with modified zeolite using (3-aminopropyl) trimethoxysilane. PBAT composites were compounded by melt mixing using twin screw extrusion then molded into film by cast film extrusion process. Effects of zeolite 13X at 1 wt% and zeolite doped potassium ion (K+) on thermal properties, permeability of gases (oxygen, carbon dioxide and water vapor) and also absorption of ethylene gas of PBAT composites films have been studied. Typically, zeolite would act as a nucleating agent. Therefore, adding zeolite would increase the degree of crystallinity of PBAT. Comparing zeolite with and without cation exchange, the degree of crystallinity in film tended to increase for the one doped with potassium ion. Either zeolite with or without potassium exchange had no impact on thermal stability of composite films. Gas permeation of PBAT/zeolite film possessed lower permeation of oxygen and carbon dioxide whereas the water vapor transmission showed relatively higher rate than the neat PBAT. After cation exchange with zeolite, the permeation of oxygen and carbon dioxide has reduced 21.04% and 21.90% respectively but the effect of K+ exchange had no effect on water vapor transmission compared with PBAT. Film of PBAT and zeolite doped with cation could absorb ethylene gas more than the one with zeolite.

1. Introduction
Low density polyethylene (LDPE) is one of the most used polymers to fabricate the fruits packaging with the drawbacks of long period of time to decompose. Researchers are interested in poly(butylene adipate-co-terephthalate) (PBAT) which is a biodegradable polymer with mechanical properties similar to LDPE. However, properties only are not enough to lengthen the fruits shelf life. There are a number of choices to extend the shelf life, for example, by improve barrier properties of food packaging using fillers like activated carbon, titanium dioxide and blending polymer [1]. In this research, adding zeolite into PBAT is one option to control oxygen (O2), carbon dioxide (CO2), water vapor and ethylene gas (C2H4) permeated through the film packaging. Normally, zeolite is used as catalyst in petroleum for selective absorbent of gaseous molecules. Zeolite13X itself has effective pore opening of 8 angstroms. Therefore, it can absorb O2, CO2, water vapor and C2H4 which have critical
diameters of 2.8, 2.8, 3.2 and 4.2 angstroms. Zeolites not only improve gas permeability of polymer but also thermal properties. However, the polarity difference of PBAT and zeolite could affect the dispersion of zeolite in polymer matrix. (3-aminopropyl)trimethoxysilane was used as the coupling agent to improve the compatibility between zeolite and PBAT. Potassium ion (K+) is one of effective gas ethylene adsorbent [2]. Potassium nitrate (KNO₃) was selected as the ethylene adsorbent to improve ethylene adsorption of zeolite. [3]

As mention earlier, researchers are focusing on development of film packaging of poly(butylene adipate-co-terephthalate) incorporated with modified zeolite using (3-aminopropyle)trimethoxysilane. Effects of zeolite 13X at 1 wt% and cation exchanged zeolite with potassium ion on thermal properties and permeability of gases (oxygen, carbon dioxide and water vapor) and also adsorption of ethylene gas of PBAT composites films have been thoroughly studied.

2. Experimental

Poly(butylene adipate-co-terephthalate), PBAT Ecoflex F blend Cl200 was used as polymer matrix. It was purchased from Polymats Co., LTD Thailand. Zeolite 13X with size of 38-45 micron and (3-aminopropyl) trimethoxy silane was purchased from Sigma-Aldrich. Potassium nitrate was purchased from Ajax Finechem. For surface functionalization of zeolite, zeolite was added to mixed solvent of methanol and deionized (DI) water 2:1 v/v with (3-aminopropyl) trimethoxy silane 1 wt% of zeolite and stirred at room temperature for 5 hours. After that reaction mixture was filtered and washed by methanol and DI water to remove non react silane. Zeolite powder was dried in over at 80°C overnight.

For preparing cation exchange of zeolite with potassium ion, 1.25 wt% solution was dissolved in DI water. Zeolite powder was mixed with potassium nitrate solution and stirred for 24 hours at room temperature. Zeolite with potassium ion exchanged was filtered, washed and dried overnight at 80°C. For preparation of PBAT/Zeolite film, PBAT and 1 wt% zeolite were compounded by twin screw extruder, SHJ-25 Enmech model, with temperature profile 120-175°C. Die temperature is 180°C at 30-45 rpm screw speed. Extrudate was cooled down to room temperature and was pelletized to obtain PBAT/Zeolite pellets and then were processed to film using cast film extruder. Temperature profile was set 135-160°C from feeder to die with 60 rpm screw speed. PBAT/zeolite films thickness were gauge-controlled into the range of 0.07 mm ± 0.02 mm.

For characterization of PBAT/zeolite film, Differential Scanning Calorimetry (DSC) DSC Perkin Elmer, were carried under nitrogen atmosphere. The sample was heated from 25°C up to 200°C at rate of 10°C/min in Heat-Cool-Heat mode. Crystallinity degree, Xc, was calculated using Equation (1) where ∆Hm is the heat of melting and ∆Hm° is the heat of fusion of 100% crystalline PBAT, considered as 114 J/g.

\[ Xc = \frac{\Delta H_m}{\Delta H_m^0} \times 100 \quad (1) \]

For oxygen and carbon dioxide permeability test, films were cut into square shape 2 inch x 2 inch then attached to gas permeation tester foil for Gas Permeation Tester (GDP-C, Brugger). Water vapor transmission rates (WPVR) of films were determined according to the standard method ASTM E96. Film samples were placed on cups containing 15 g of silica gel and place in desiccators contain NaCl solution to control humidity 75% RH. Cups were weighed every hour for nine hour and then every 24 hours until cups had constant weight. For ethylene adsorption testing, films were prepared into square shape 5 inch x 5 inch then were placed into 10 ml of container which saturated with 5 ppm of ethylene gas. Sampling 2 ml of ethylene gas from container using syringe then testing using Gas chromatography - Mass spectroscopy using Flame Ionization Detector (FID) mode, carrier gas is helium with flow gas rate and temperature is 1.20 ml/min and 40°C respectively.

3. Results and discussion
3.1. Thermal properties of film
Table 1 shows the melting temperature (T_m) and % crystallization (X_c) of PBAT film. PBAT has % crystallinity 8.16% while PBAT with zeolite 13X has higher percentage of crystallinity than PBAT. This is due to zeolite acting as nucleating agent. Regarding the effect of zeolite treatment by doping K+, crystallinity of PBATZ13X_1%_K+ was lower than the one of PBAT composite but higher than the one of neat PBAT. The tabulated data implied the treated K+ zeolite could act as nucleating agent when compared crystallinity with neat PBAT. Naturally, zeolite 13X composed of sodium ion (Na+) in the structure. Treated zeolite 13X by doping potassium ion (K+) lessened the capability as nucleating agent. This could be the fact of potassium ion 1.33 angstrom as compared to sodium ion size of 0.97 angstrom. And thus treated zeolite with doping potassium ion possesses less surface area for crystallinity induction of PBAT. In addition, it is found that melting temperature of PBAT composite was lower than the one of neat PBAT. This might be more crystals nucleated by zeolite in the polymer composite. Thus the crystal size of PBAT composite would be smaller than the neat PBAT which then affected the lower T_m. However, modified zeolite with potassium ion had no effect on melt temperature of PBAT.

| Sample         | T_m (°C) | Delta H (°C) | X_c (%) |
|----------------|----------|--------------|---------|
| PBAT           | 121.5    | 9.31         | 8.16    |
| PBATZ13X       | 119.8    | 18.01        | 15.80   |
| PBATZ13X_K+    | 119.7    | 11.11        | 9.74    |

3.2. Barrier properties of film
Table 2 shows permeation of oxygen and carbon dioxide through PBAT composite film compared with neat PBAT. Adding zeolite into PBAT will reduce the permeability of oxygen and carbon dioxide due to zeolite particles created the longer pathway for gases to diffuse through the film. Moreover, zeolite pores could absorb gases with smaller molecules than the pore sizes. Therefore, permeation rate of both oxygen and carbon dioxide through film were decreased. In addition, crystalline of polymer could affect the permeation rate. More crystalline phase could reduce the rate of gas permeability through tested film [4]. Regarding the effect of cation exchange in zeolite, PBAT films incorporated with modified zeolite had both of oxygen and carbon dioxide permeation rates lower than unmodified zeolite. This could be explained by the reduction of pore size from the introduction of potassium ion of which diameter was larger than sodium (Na+) ion. Potassium ion could form donor-acceptor complexes or pi-complexes with oxygen and carbon dioxide. Potassium ion doped in modified zeolite 13X had likely to have natural affinity with oxygen and carbon dioxide rather than sodium ion in such modified zeolite and thus it illustrated more effectiveness on permeability of both oxygen and carbon dioxide gases through PBAT film.

| Sample         | O2 permeability (cm·mm·m2·atm) | O2 permeability (barrer) | CO2 permeability (cm·mm·m2·atm) | CO2 permeability (barrer) |
|----------------|--------------------------------|--------------------------|---------------------------------|--------------------------|
| PBAT           | 182.17                         | 2.77                     | 917.15                          | 13.97                    |
| PBATZ13X       | 151.78                         | 2.31                     | 826.77                          | 12.59                    |
| PBATZ13X_K+    | 143.83                         | 2.19                     | 744.09                          | 11.33                    |

Water vapor transmission rate (WVTR) of PBAT composites films were shown in Table 3. Neat PBAT film possessed lower water vapor transmission rate than PBAT composite film. This could be the lower hydrophilicity of PBAT compared to zeolite which composed of silica and alumina in which the pore structures were made. These pores will allow those smaller molecules to pass through. In this
case, water molecular size of 3.2 angstrom with bending shape molecule can diffuse through zeolite in PBAT better than neat PBAT. Diffusion and adsorption abilities depend on many factors. One of important factors is so called active surface area. [5] Zeolite 13X is approximately 8 angstrom of pore size. Zeolite 13X possesses higher surface area which can lead to high ability of water adsorption by hydrogen bonding between water molecule and zeolite. However, PBAT film incorporated with modified zeolite 13X with doping K+ had not much difference in WVTR. Therefore, PBAT film incorporated with zeolite 13X spent less time in order to diffuse through film compare to neat PBAT.

**Table 3 WVTR and percentage of ethylene gas absorption by PBAT films.**

| Sample       | WVTR (g/m² day) | % Ethylene gas absorption |
|--------------|-----------------|---------------------------|
|              |                 | Day 2 | Day 3 | Day 7 | Day 14 |
| PBAT         | 33.83           | 4.00  | 21.86 | 34.88 | 49.35  |
| PBATZ13X     | 44.92           | 11.99 | 26.19 | 36.46 | 52.52  |
| PBATZ13X_K+  | 45.95           | 25.40 | 35.00 | 43.94 | 53.34  |

Table 3 shows the barrier property of ethylene gas absorption of neat PBAT compared with PBAT composite film of 2-14 days. Fruits and vegetables would normally release ethylene gas resulting in premature ripening. If packaging film could absorb the ethylene gas, it would highly likely prolong the shelf life of packaged products. PBAT composite film in cooperative with modified zeolite by potassium ion could certainly absorb more ethylene gas than PBAT composite and neat PBAT, respectively. This could be explained by the formation of pi complex between ethylene gas and K+ ion. Alkene from ethylene which acts as electron donor can donate its pi bonding electron to metal or so called electron acceptor.

4. Conclusion

This research focused on the effect of modified zeolite on thermal and barrier properties of biopolymer film made of PBAT. From DSC results, zeolite itself would initiate a higher percentage of crystallinity in PBAT film because zeolite could act as nucleating agent. The results of permeability test of O₂ and CO₂ indicated that zeolite 13X caused the PBAT film to possess a relatively lower O₂ and CO₂ permeability than the neat PBAT. In addition, PBAT incorporated with zeolite 13X led to higher ability of ethylene gas absorption thorough PBAT film. Regarding the treated zeolite 13X by doping potassium ion in PBAT film, PBAT film with treated potassium ion zeolite had no effect in melting temperature but it would have the effect on decrement of crystallinity. Percent crystalline of PBATZ13X_K+ would be decreased once compared with PBAT film with untreated K+. The results of permeability test of O₂ and CO₂ indicated that treat K+ zeolite 13X had the effect on PBAT film of lowering both of O₂ and CO₂ permeability once compared with film of untreated K+ zeolite. In regards to the water vapor transmission, zeolite with K+ exchange had no significant effect on WVTR. This might be because the pore size play more significant role than the cation exchange effect.

5. References

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