

CHAPTER VI
PHYSICAL PROPERTIES AND BARRIER PROPERTIES
OF pH INDICATOR NANOCOMPOSITE FILMS

6.1 Abstract

The colorimetric indicator for detecting fish and climacteric fruit freshness was prepared based on polypropylene/chromophores (methyl red) modified functionalized PCH nanocomposite films and low density polyethylene/chromophores (bromothymol blue) modified PCH nanocomposite films. The nanocomposites were prepared by melt mixing process through the twin screw extruder. Sodium-neutralized ethylene-co-methacrylic acid (Surlyn[®]) was used as a compatibilizer to improve the dispersion of porous material in polymer matrix. The crystallization temperature and % crystallinity of PP/APPCH-MR nanocomposites was higher than neat PP. While the crystallization temperature of LDPE/PCH-BTB nanocomposites remained constant. The nanocomposites showed the higher thermal stability than neat PP and LDPE. The nanocomposite films showed the improvement of oxygen gas barrier property due to porous material providing tortuous path in the film.

Keyword: Nanocomposite/ Porous materials

6.2 Introduction

Polypropylene (PP) and polyethylene (PE) are the examples of the widely used plastics in large volume because of the advantage such as low cost and wide range of application. To overcome the disadvantage of PP and PE such as low service temperature and to enhance the thermal stability, trying to improve their properties with nanotechnologies was necessary.

Due to the advantages over other traditional materials such as barrier properties, the use of clay filler in polymer nanocomposite as food packaging

materials has increased. In order to improve the barrier properties, clay-polymer nanocomposites are based on a tortuous path around the clay plates, forcing the gas permeation to travel a longer path to diffuse through the film. The increase in path length is a function of the high aspect ratio of the clay filler. Moreover, the resulting from using clay nanoparticles including increased the mechanical properties and thermal properties in polymer.

Clay/polymer nanocomposites are the mixtures of clay in organic polymer. But the homogeneous dispersion of clay in organic polymers is not easy due to the hydrophilicity of clay surface and hydrophobicity of polymer such as polypropylene and polyethylene. Therefore, compatibilizer is important factor to improve the compatibility between polymer and clay.

Previous chapters were reported the successfully synthesized chromophores modified porous clay and fabricated the nanocomposite films by mixing with thermoplastics. Consequently, in this chapter, those nanocomposite films were further investigated the mechanical properties of the films, thermal behaviors including the gas barrier properties which are one of the requirements for food packaging.

The pH indicator nanocomposite films developed from this research work will be applied as an innovative packaging. The practical use can be prepared as a label film attached on food packaging.

6.3 Experimental

A. Preparation of PP/APPCH-MR Nanocomposite Film

The nanocomposite was prepared by using twin-screw extruder (Labtech) with $L = 80$ and $D = 20$ mm. The operation temperature was performed at 170, 175, 180, 185, 190, 195, 200, 205, 210 and 215°C from hopper to die respectively and the screw speed was 50 rpm.

First, polypropylene (PP) was blended with 6%wt surlyn[®] in order to obtain PP/surlyn[®] pellet. Then, PP/surlyn[®] pellet was mixed with 2%wt of chromophores modified functionalized PCH to obtain the nanocomposite. Each composition was dried in vacuum oven for moisture removal and premixed in tumble mixer before

extruded through the twin screw extruder. Then, the extruded nanocomposite was quenched immediately in water and pelletized. The obtained pellet was dried in vacuum oven.

Nanocomposite films of PP/chromophores modified functionalized PCH was prepared by compression molding machine at 5 tons of force for 5 minutes. The processing temperature was 210°C.

B. Preparation of LDPE/PCH-BTB Nanocomposite Films

The nanocomposite was prepared by using twin-screw extruder (Labtech) with $L = 80$ and $D = 20$ mm. The operation temperature was performed at 130°C from hopper to die respectively and the screw speed was 25 rpm.

First, low density polyethylene (LDPE) was blended with 6%wt surlyn[®] in order to obtain LDPE/surlyn[®] pellet. Then, LDPE/surlyn[®] pellet was mixed with 2 %wt of chromophores modified PCH to obtain the nanocomposite. Each composition was dried in vacuum oven for moisture removal and premixed in tumble mixer before extruded through the twin screw extruder. Then, the extruded nanocomposite was quenched immediately in water and pelletized. The obtained pellet was dried in vacuum oven.

Nanocomposite films of LDPE/chromophores modified PCH was prepared by compression molding machine at 5 tons of force for 5 minutes. The processing temperature was 130°C.

C. Characterizations

Thermogravimetric analysis (TGA) was used to study the thermal stability of PP/APPCH-MR nanocomposite and LDPE/PCH-BTB nanocomposite compared to PP and LDPE. The degradation temperature of samples was determined by Perkin Elmer Pyris Diamond TG/DTA instrument. The pellets were loaded on platinum pan and heated from 30 to 900°C at heating rate 10°C/min and flow under N₂ 200 ml/min.

The crystallization and melting behavior of PP/APPCH-MR nanocomposite and LDPE/PCH-BTB nanocomposite compared to PP and LDPE were measured by Differential Scanning Calorimeter (DSC) using Met.ler DSC822 STARe System. First, the pellet samples was heated from 30°C to 200°C at heating rate of 10°C/min in order to eliminate the influence of thermal history and then cooled down from

200°C to 30°C to observe melt crystallization behavior. After that, reheated to 200°C to observe melting behavior.

The crystallinity of samples was calculated by this equation,

$$\% \text{ Crystallinity} = \frac{\Delta H_{\text{sample}}}{\Delta H^{\circ}} \times 100$$

Where, ΔH_{sample} = enthalpy of fusion of the sample (J/g)
 $\Delta H^{\circ}_{\text{PP}}$ = enthalpy of fusion of completely crystalline (209 J/g)
 $\Delta H^{\circ}_{\text{LDPE}}$ = enthalpy of fusion of completely crystalline (293 J/g)

Tensile test of nanocomposite films was measured under ASTM D 683. The specimen was cut into rectangular shape with 10x100 mm and cross head speed of 50 mm/min.

Oxygen Permeation Tester, Illinois model 8000, was used to determine the oxygen gas transmission rate through PP sheets, PP/APPCH-MR nanocomposite sheets, LDPE sheets and LDPE/PCH-BTB nanocomposite sheets. Gas permeation experiment was investigated following the procedure described in ASTM D 3985-05 at 23°C. The films were prepared by compression molding and were cut into circular shape with 15 cm in diameter.

6.4 Result and Discussion

A. Thermal Behavior of Nanocomposites

The crystallization temperature and melting temperature were measured by DSC. The result showed that the crystallization temperature and % crystallinity of PP/APPCH-MR nanocomposites was higher than neat PP. A possible reason might be due to the porous clay acting as the nucleating agent for crystallization of PP [1]. While the crystallization temperature of LDPE/PCH-BTB nanocomposites remained constant. The melting temperature of PP/APPCH-MR nanocomposites gradually increased compared to neat PP while melting temperature of LDPE/PCH-BTB nanocomposites closed to neat LDPE. Moreover, the results indicated that the

crystalline and melting characteristics of nanocomposites not dependent on dye content. Differential scanning calorimeter thermograms of nanocomposites are shown in Figure 6.1 and 6.2.

The thermal degradation temperature was measured by TGA. TG-DTA curves were shown in Figure 6.3 and 6.4. The results showed that the thermal degradation occurred in single stage. The nanocomposites showed the higher thermal stability than neat PP and LDPE. This behavior may be attributed to the formation of a high-performance carbonaceous silicate char build up on the surface [2].

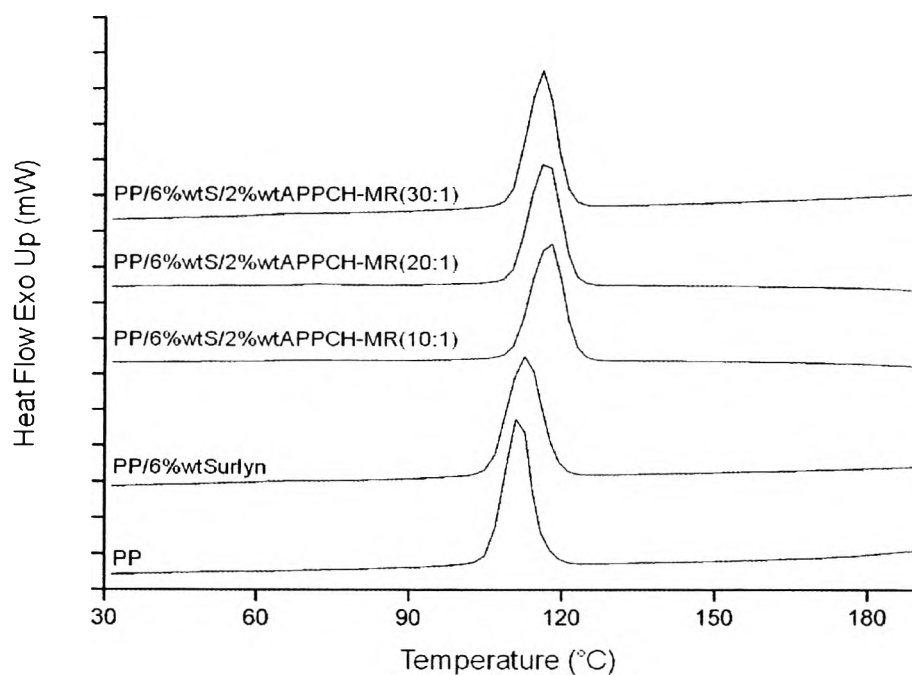
Melting, crystallization and thermal behavior results are shown in Table 6.1 and 6.2.

Table 6.1 Melting and Crystallization behavior

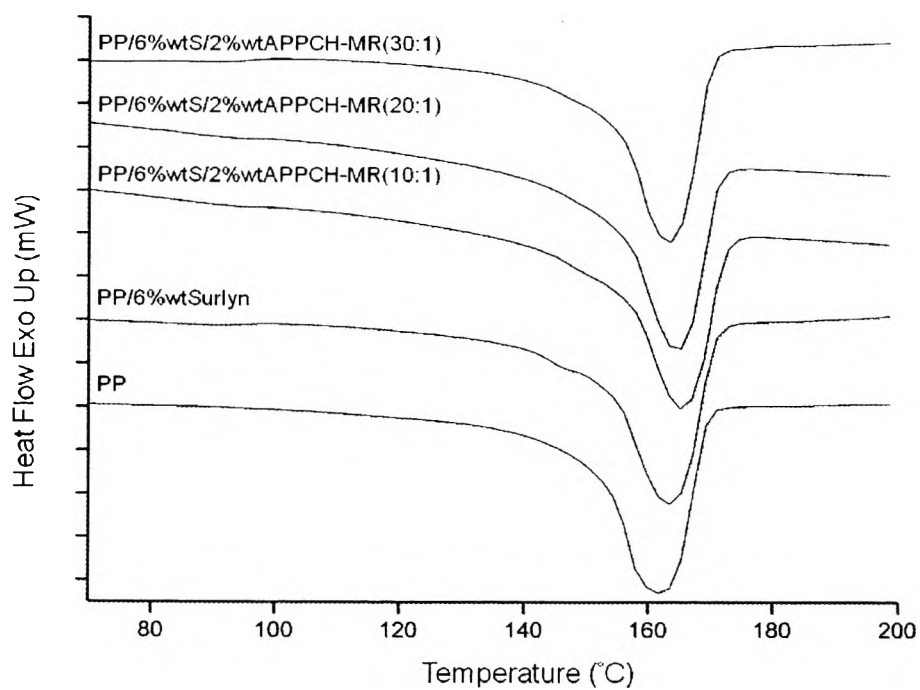
Sample	T _c (°C)	T _m (°C)	ΔH _m (J/g)	%Crystallinity
PP	111.56	161.96	69.58	33.29
PP/6%wtSurlyn	112.78	163.28	76.67	36.68
PP/6%wtS/2%wtAPPCH-MR(10:1)	117.58	165.34	70.52	33.74
PP/6%wtS/2%wtAPPCH-MR(20:1)	116.97	164.43	71.46	34.19
PP/6%wtS/2%wtAPPCH-MR(30:1)	116.31	163.34	71.08	34.01
LDPE	95.01	109.10	69.58	33.29
LDPE/6%Surlyn	95.22	109.31	76.67	36.68
LDPE/6%wtS/2%wtPCH-BTB(10:1)	95.78	108.76	70.52	33.74
LDPE/6%wtS/2%wtPCH-BTB(20:1)	95.28	109.27	71.46	34.19
LDPE/6%wtS/2%wtPCH-BTB(30:1)	95.57	109.29	71.08	34.01

Table 6.2 Thermal behavior

Sample	Char residue (%wt)	T _d (°C)
PP	0	427.3
PP/6%wtSurlyn	0	441.6
PP/6%wtS/2%wtAPPCH-MR(30:1)	2.6	439.2
LDPE	1.2	449.0
LDPE/6%Surlyn	0.2	450.7
LDPE/6%wtS/2%wtPCH-BTB(10:1)	2.9	451.9
LDPE/6%wtS/2%wtPCH-BTB(20:1)	5.0	449.0
LDPE/6%wtS/2%wtPCH-BTB(30:1)	2.6	453.0

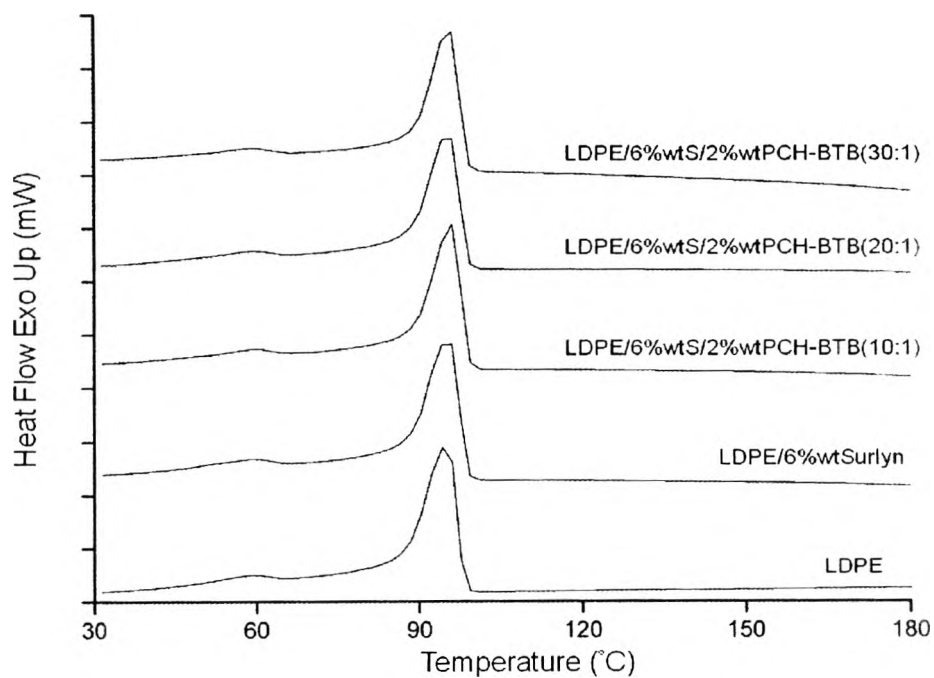


(a)

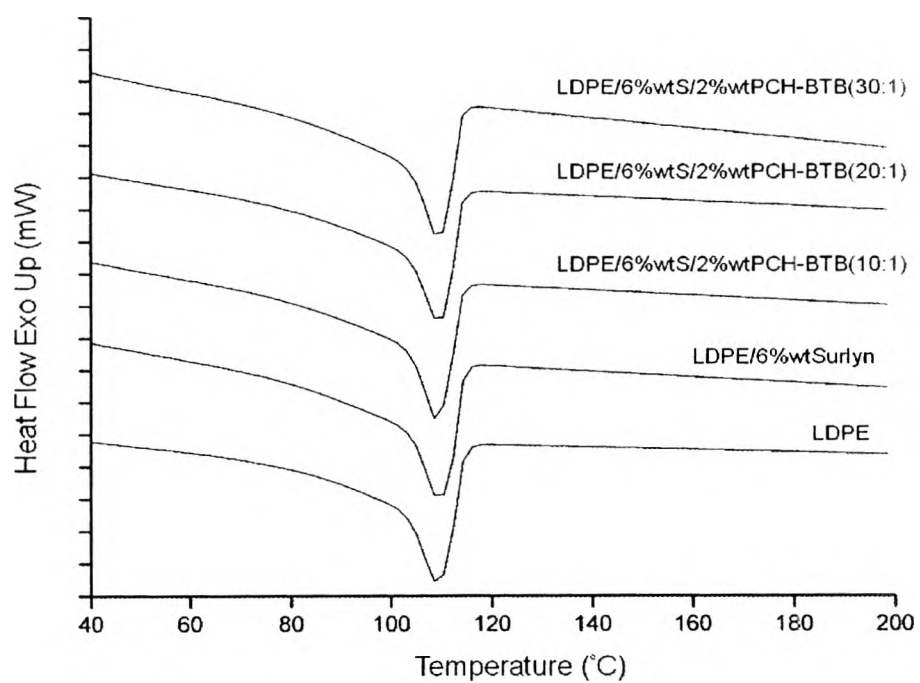


(b)

Figure 6.1 DSC thermograms of PP/APPCH-MR nanocomposites (a) crystallization temperature and (b) melting temperature.



(a)



(b)

Figure 6.2 DSC thermograms of LDPE/PCH-BTB nanocomposites (a) crystallization temperature and (b) melting temperature.

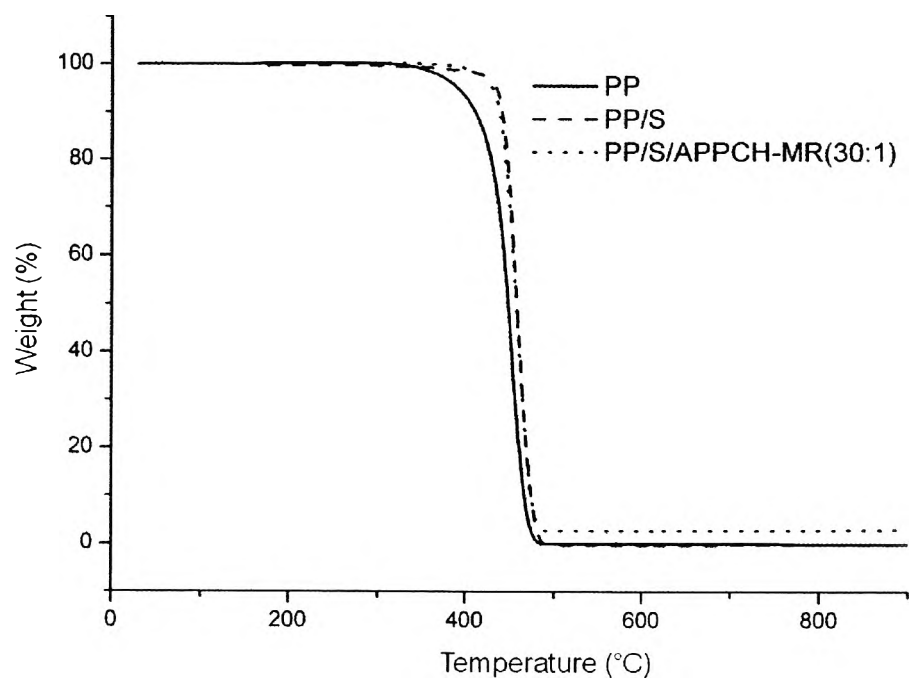


Figure 6.3 TG curves of PP/APPCH-MR nanocomposites.

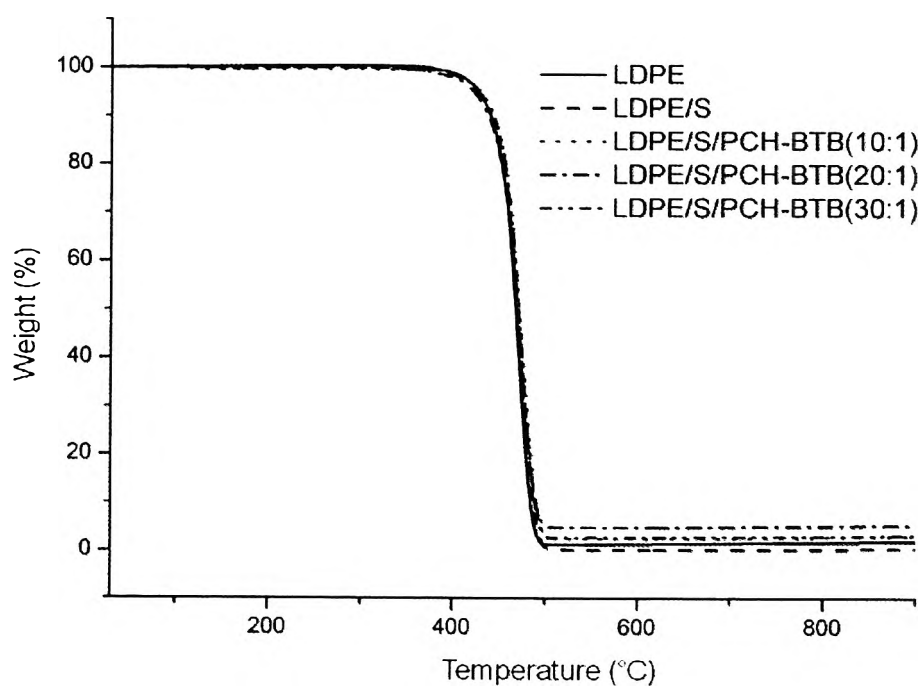


Figure 6.4 TG curves of LDPE/PCH-BTB nanocomposites.

B. Mechanical Properties of Nanocomposites

The mechanical properties of PP/APPCH-MR nanocomposite films compared to neat PP were shown in Figure 6.5, 6.6 and 6.7. The result showed that young's modulus, tensile strength and % elongation at yield decreased in nanocomposite films compared to neat PP. Young's modulus of nanocomposite film decreased compared to PP films. The occurrence could be explained by not uniformly disperse of clay in nanocomposite films. In addition, the tensile strength reduced due to it loses the ability to transfer stress. % Elongation at yield decreased because clay obstructed the movement of PP along the applied force [3-5].

The mechanical properties of LDPE/PCH-BTB nanocomposite films compared to neat LDPE were shown in Figure 6.8, 6.9 and 7.0. The result showed that young's modulus and tensile strength increased in the presence of clay in nanocomposite films due to the porous clay acting as the excellent filler with enable to reinforce the films. While % elongation at yield decreased in the presence of clay in nanocomposite films. The possible reason may be due to the addition of clay was attributed to increase stiffness of polymer [6].

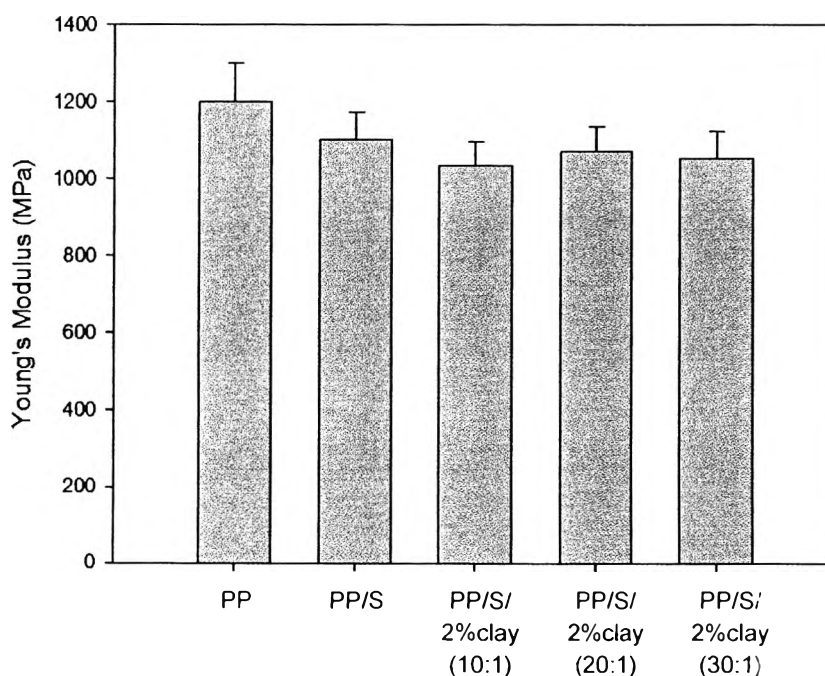


Figure 6.5 Young's Modulus of PP and PP/APPCH-MR nanocomposite films.

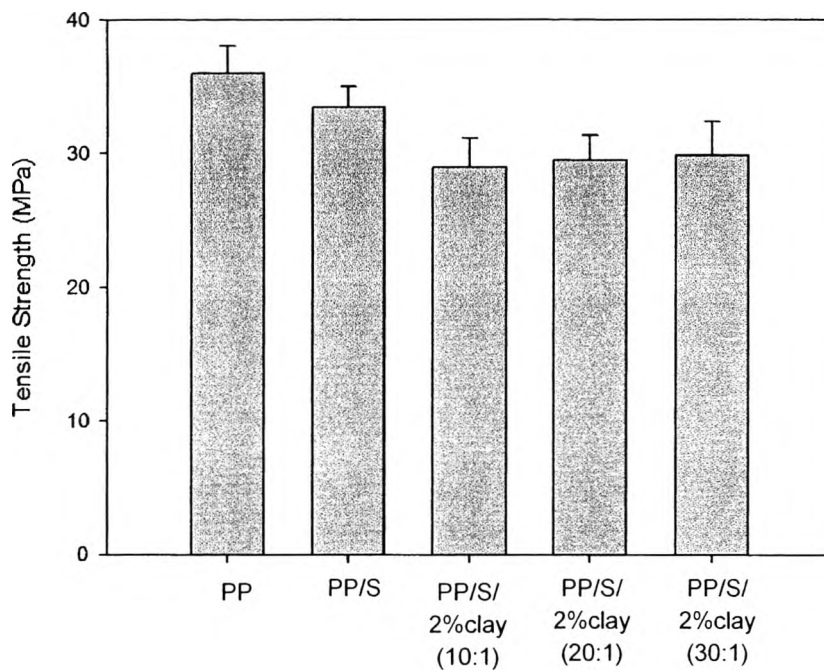


Figure 6.6 Tensile Strength of PP and PP/APPCH-MR nanocomposite films.

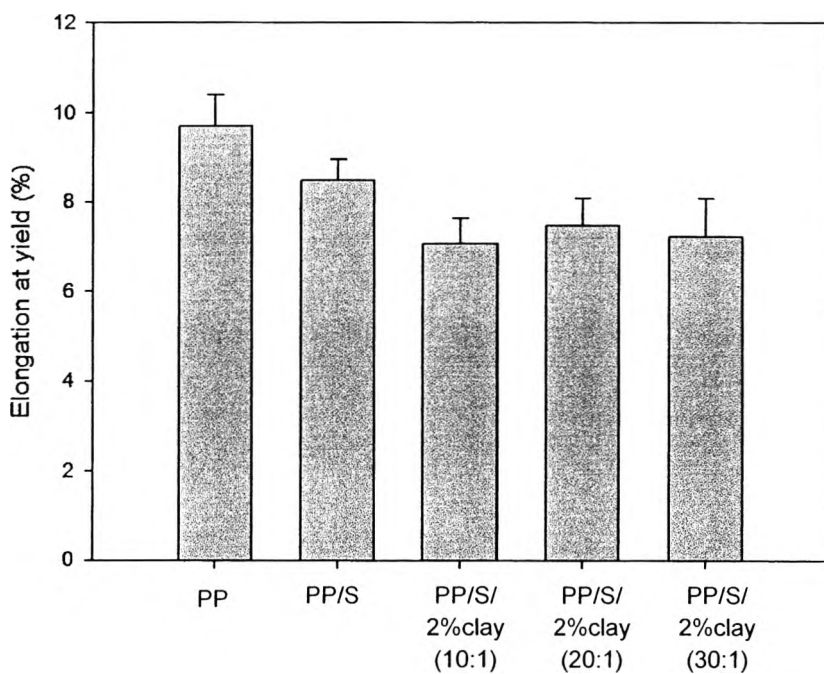


Figure 6.7 % Elongation at yield of PP and PP/APPCH-MR nanocomposite films.

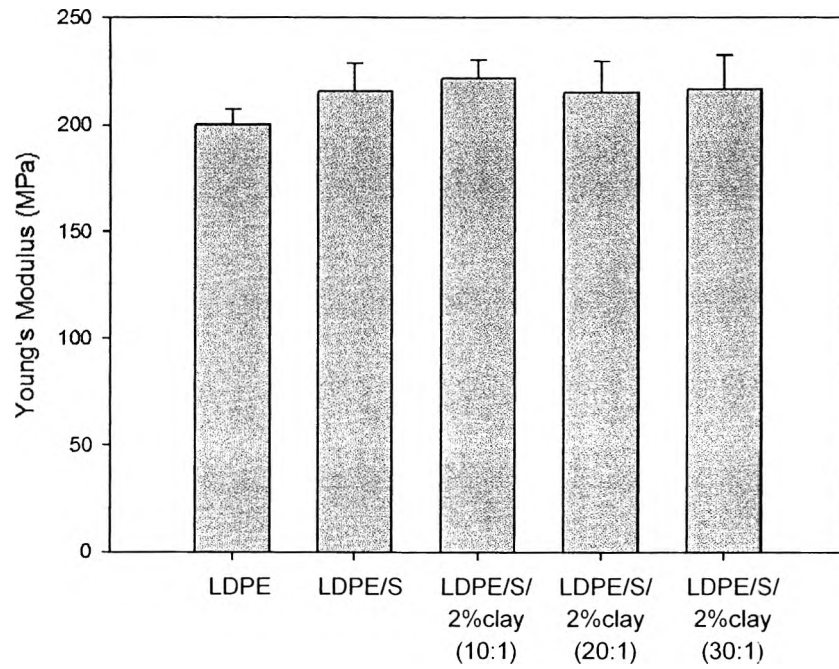


Figure 6.8 Young's Modulus of LDPE and LDPE/PCH-BTB nanocomposite films.

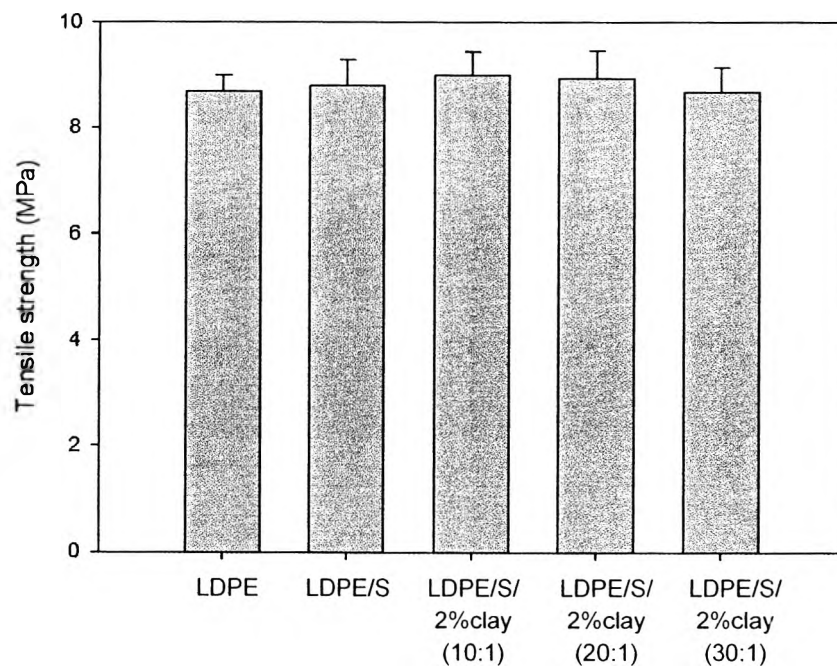


Figure 6.9 Tensile strength of LDPE and LDPE/PCH-BTB nanocomposite films.

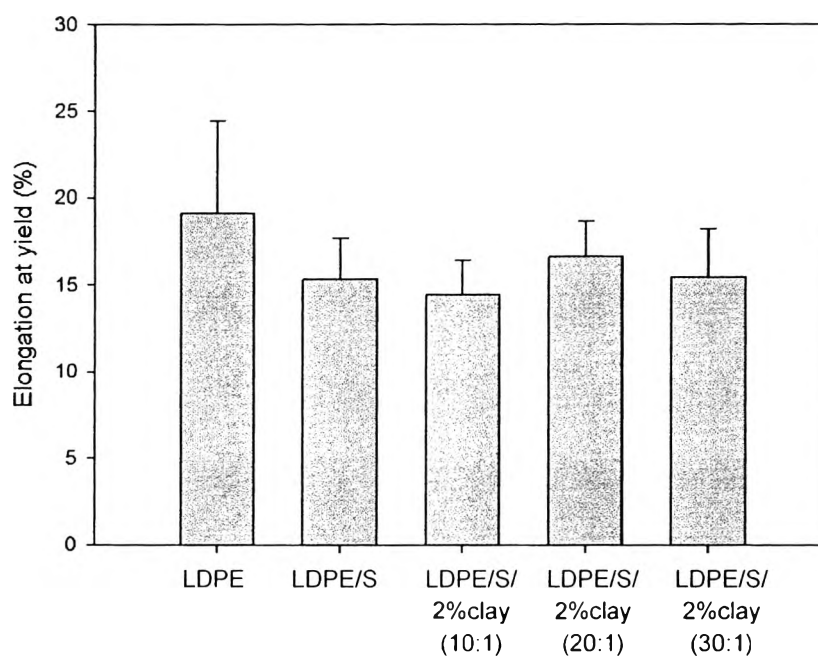


Figure 6.10 %Elongation at yield of LDPE and LDPE/PCH-BTB nanocomposite films.

C. Oxygen Gas Permeability of nanocomposite films

Oxygen gas transmission rate of nanocomposites was shown in Table 6.3 and 6.4. The results showed the reduction of oxygen transmission rate in nanocomposites compared to neat PP and LDPE. Porous clay improved the barrier properties of nanocomposite indicated by the reduction of oxygen transmission rate in the nanocomposites. The improvement in barrier properties of nanocomposites was due to the presence of porous clay which provided the tortuous path in polymer matrix.

Table 6.3 Oxygen gas transmission rate of PP and PP/APPCH-MR nanocomposites

Sample	Oxygen gas transmission rate (cc/m ² .day)
PP	148
PP/APPCH-MR (30:1)	140

Table 6.4 Oxygen gas transmission rate of LDPE and LDPE/PCH-BTB nanocomposites

Sample	Oxygen gas transmission rate (cc/m ² .day)
LDPE	257
LDPE/PCH-BTB (10:1)	225
LDPE/PCH-BTB (30:1)	230

6.5 Conclusion

pH indicator films prepared by PP/APPCH-MR and LDPE/PCH-BTB nanocomposites was investigated both of mechanical properties and thermal stability. Both nanocomposites showed the higher thermal stability and improvement in oxygen barrier properties due to the presence of porous clay in nanocomposite.

6.6 Acknowledgements

This work was supported by the Higher Education Research Promotion and National Research University Project of Thailand, Office of the Higher Education Commission (FW 0649A) and Ratchadaphiseksomphot Fund. Partial funding was received from the Polymer Processing and Polymer Nanomaterials Research Unit, the Petroleum and Petrochemical College, Chulalongkorn University and the Center of Excellence on Petrochemical and Materials Technology (PETRO-MAT).

6.7 Reference

- 1 Ding, C., Jia, D., He H., Guo, B. and Hong, H. (2005). How Organo-montmorillonite Truly Affects the Structure and Properties of Polypropylene. Polymer Testing, 24, 94-100.

- 2 Modesti, M., Lorenzetti, A., Bon, D. and Besco, S. (2006). Thermal Behavior of Compatibilised Polypropylene Nanocomposite: Effect of Processing Conditions. Polymer Degradation and Stability, 91, 672-680.
- 3 Tassanawat, S., Manuspiya, H., Magaraphan, R. and Nithithanakul, R. (2007). Polypropylene/Organoclay Nanocomposite for pH-sensitive Packaging. M.S. Thesis, The Petroleum and Petrochemical Collage, Chulalongkorn University, Bangkok, Thailand.
- 4 Seephueng, A., Manuspiya, H. and Magaraphan, R. (2008). Smart Packaginfg for Fish Spoilage Indicator. M.S. Thesis, The Petroleum and Petrochemical Collage, Chulalongkorn University, Bangkok, Thailand.
- 5 Othman, N., Ismail, H., and Mariatti, M. (2006). Effect of Compatibilizers on Mechanical and Thermal Properties of Bentonite Filled Polypropylene Composites. Polymer Degradation and Stability, 91, 1761-1774.
- 6 Santamaria, P. and Eguiazabal, J. I. (2012). Structure and Mechanical Properties of Blown Films of Ionomer-compatibilizerd LDPE Nanocomposites. Polymer Testing, 31, 367-374.