

CHAPTER V
MODIFICATION OF POROUS CLAY HETEROSTRUCTURES (PCHs) AND
HYBRID ORGANIC-INORGANIC PCHs (HPCHs) NANOCOMPOSITES
FOR ETHYLENE ENTRAPPING SYSTEM

5.1 ABSTRACT

Polypropylene/porous clay heterostructures (PP/PCHs) nanocomposites were prepared via direct melt intercalation by twin screw extruder. Surlyn ionomer was used as a compatibilizer to improve the dispersion of porous clay in PP matrix. The PCHs were synthesized by the self-assembly of silica framework around surfactant templates intercalated within the galleries of Na-bentonite clay host. Before the synthesis, pH of the bentonite clay was adjusted to 4 conditions including pH 9, 7, 5 and 3. Moreover, the chemical property of these mesoporous materials was capable of modifying via the incorporation of methyl group into silica framework to obtain hybrid organic-inorganic PCHs (HPCHs), providing more hydrophobicity on the porous structures. After obtaining the porous clay, these porous materials were utilized as the inorganic filler in PP nanocomposites. Subsequently, they were fabricated to thin film by tubular blown film extrusion machine. The nanocomposites were characterized by using XRD, DSC and TG-DTA. The ethylene permeability of PP/PCHs and PP/HCHs nanocomposites films were measured to evaluate the potential use in active packaging application as an ethylene scavenger film.

keyword : porous clay heterostructures, polypropylene, nanocomposites, ethylene permeability, ethylene scavenger.

5.2 INTRODUCTION

Polypropylene (PP) is one of the most widely used plastics in large volume and a fast growing thermoplastic that dominated the industrial applications because it is relatively inexpensive, easily modified to meet a wide range of thermal and mechanical requirements and suitable for virtually all kinds of processing equipment. However, there are many disadvantages such as low toughness and low service temperature [1].

Recently, there has been a growing interest in the development of polymer-clay nanocomposites. Nanocomposites constitute a new class of material that involves nano-scale dispersion in a matrix. Nanocomposites have at least one ultrafine phase dimension, typically in the range of 1–100 nm, and exhibit improved properties when compared to micro- and macro-composites. Strong interfacial interactions between the dispersed clay layers and the polymer matrix lead to enhanced mechanical, thermal and barrier properties of the virgin polymer [2]. The most commonly used clay to prepare nanocomposite is from the smectite group, such as montmorillonite (MMT). In this clay mineral the silicate layers are joined through relatively weak dipolar and Van der Waals forces and the cations Na^+ and Ca^{2+} located in the interlayers. These cations can be replaced by organic cations such as alkylammonium ions through an ionexchange reaction to provide an organophilic silicate. Nanocomposite can be obtained by direct polymer melt intercalation, where polymer chains are spread into the space between the clay layers and this can be done by conventional polymer processing techniques such as extrusion [3].

Many research efforts focus on the preparation of polypropylene-clay nanocomposites. But PP does not include any polar groups in its backbone, it was thought that the homogeneous dispersion of the silicate layers in PP would not be realized. Hence, it is frequently necessary to use a compatibilizer such as maleic anhydride modified polypropylene (PP-g-MA) and surlyn ionomer [4]. Surlyn is a commercial thermoplastic ionomer resin used in the packaging industry. It is excellent for packaging applications due to its sealing performance, formability, clarity, oil-grease resistance and high hot draw strength. Good hot draw strength allows faster packaging line speeds and reduces packaging failures. Structure property relationships for nanocomposites formed by melt processing from a series of organoclays and poly(ethylene-co-methacrylic acid) ionomers are studied [5].

The synthesis of porous materials has attracted much interest since they offer many advantages as adsorbents, gas separation devices or gas-storage materials [6]. Recently, the discovery of a new class of porous materials known as porous clay heterostructure (PCH) has been proposed [7]. The PCH materials reveal important properties such as exhibiting high surface areas with uniform and specific pore sizes in the rarely observed supermicropore to small mesopore region [8]. In the synthesis

of a PCH, layered clays are first intercalated with cationic surfactants. Neutral amine co-surfactant molecules are then intercalated along with silica species which leads to polymerize surrounding the surfactant micelles in the galleries. Then, an open-framework of silica is formed in the galleries after surfactant removal [9]. Moreover, the chemical properties of these mesoporous materials are capable of modifying via the incorporation of organic components. From this viewpoint, these porous materials could find application in many fields. Both PCHs and HPCHs materials are capable of utilizing as inorganic particles in polymer nanocomposites owing to their structures still remain as clay galleries.

The objective of the present study is to find a new application of the PCHs and HPCHs materials in the field of food packaging as ethylene scavenger film due to the presence of uniform and specific porous structure providing high surface area. In addition, they can be improved ethylene adsorption capacity by the incorporation of methyl groups enhancing hydrophobic surface in the HPCHs materials.

5.3 EXPERIMENTAL

Materials

Na-Bentonite (BTN), (Mac-Gel® GRADE SAC), was obtained from Thai Nippon Chemical Industry Co., Ltd. The cation exchange capacity (CEC) of BTN is 43 mmol/100g of clay.

Cetyltrimethylammonium [$C_{16}H_{33}N^+(CH_3)_3$] bromide (CTAB), Tetraethyl orthosilicate (TEOS), $Si(OC_2H_5)_3$ and Methyltriethyl orthosilicate (MTS), $CH_3Si(OC_2H_5)_3$ were purchased from Fluka. Dodecylamine, $C_{12}H_{27}N$, (98% purified) was supplied by Aldrich. Methanol (CH_3OH) was supplied by Lab Scan and Hydrochloric acid (HCl) was supplied by Carlo Erba.

Polypropylene (PP), under trademark Moplen HP550R, was a blow film extrusion grade polymer (MFI = 11) supplied by HMC polymers Co., Ltd. Sodium-neutralized poly(ethylene-co-methacrylic acid) ionomer (Surlyn® PC350, 4.5 MFI) was purchased from DuPont.

Purification and pH Adjustment of Bentonite Clay

Na-bentonite (BTN) was pulverized and sieve through 325 mesh. Four 10-g of the passing part were purified by centrifugation and then washed with distilled water several times until pH value was near 9. After that, centrifugation was applied. Again, the same amount of distilled water was added, and then the pH of three samples was adjusted to 3, 5, and 7 by using dilute HCl solution. This procedure was repeated for three days to equilibrate the pH of each sample. The samples were air-dried overnight and again pulverized in a mortar.

Formation of Porous Clay Heterostructures (PCHs)

Each 3 g of pH-adjusted bentonite was converted into a quaternary ammonium form by ion exchange with 50 ml of 0.1 M aqueous cetyltrimethylammonium bromide and stirred at 50 °C for 24 h. After the reaction time, the solid was filtered out, washed with a mixture of methanol and water and then air-dried. The obtained organoclay was stirred in dodecylamine for 30 min at 50°C. In addition, TEOS (at molar ratio of organoclay:dodecylamine: TEOS was

1:20:150) was added and the resulting suspension was stirred for further 4 h at room temperature. The solid was separated from solution again by filtration and air-dried overnight at room temperature to form the as-synthesized PCHs. The surfactant was removed from the as-synthesized PCHs by solvent extraction using methanol/HCl solution. Typically, 1 g of the as-synthesized PCHs material has been added to 45 mL of methanol and 5 mL of HCl and refluxed for 2 h. The solid was subsequently filtrated out and washed with a mixture of methanol and water and dried at 70°C under vacuum for 2 hr. The obtained PCHs are named PCH-n (n denotes the pH value of pH-adjusted bentonite clay).

Modification of Hybrid Organic-Inorganic Porous Clay Heterostructures (HPCHs)

The pH-adjusted bentonite was converted into a quaternary ammonium exchange form to obtained organoclay and reacted with dodecylamine according to PCHs formation procedure previously. Then a mixture of TEOS and MTS in a mole fraction of 1:1 was added and stirred for further 12 h at 35 °C. The obtained as-synthesized organic modified PCHs (HPCHs) were collected by centrifugation and air-dried overnight at room temperature. The surfactant was removed from the as-synthesized HPCHs by solvent extraction using methanol/HCl solution as same procedure as in case of PCHs formation. The obtained HPCHs are named HPCH-n (n denotes the pH value of pH-adjusted bentonite clay).

Preparation of PP Nanocomposites

1 wt% PCH-n or HPCH-n, 2 wt% Surlyn ionomer and PP were melt blended in a Model T-20 co-rotating twin-screw extruder (Collin) with L/D=30 and D=25 mm; the processing conditions were the following: temperature (°C): 80, 160, 180, 195, 205, and 215 from hopper to die, respectively and the screw rotation is 50 rpm. Each composition was premixed in a tumble mixer before introducing into the twin-screw extruder to be well mixed and extruded through a single strand die, and solidified with cold water and then pelletized. The obtained pellet was dried in oven prior to blow film extrusion.

Fabrication of Thin Film Nanocomposites

The nanocomposites films were prepared by tubular blown film extrusion machine. The nanocomposites pellets were dried in oven prior to blowing. Following extrusion conditions were employed, the rotation speed of screw less than 50 rpm and blowing ratio of 0.65. The barrel and mold temperature were 210 °C. The thickness of the films was controlled to about 30 μm .

Physical Measurements

X-ray diffraction patterns were measured on a Rigaku Model Dmax 2002 diffractometer with Ni-filtered Cu K_{α} radiation operated at 40 kV and 30 mA. The nanoconposite films were observed on the 2θ range of 2-20 degree with a scan speed of 5 degree/min and a scan step of 0.02 degree.

TG-DTA curves were collected on a Perkin-Elmer Pyris Diamond TG/DTA instrument. The sample was loaded on the platinum pan and heated from 30°C to 700°C at a heating rate of 10°C/min under N_2 flow.

DSC analysis were carried out using a Perkin-Elmer DSC 7 instrument. The sample was first heated from 30°C to 200°C and cooled down at a rate of 10°C/min under a N_2 atmosphere with a flow rate of 60 ml/min. The sample was then reheated to 200°C at the same rate.

Gas permeation experiments were investigated by Brugger Gas Permeability Tester. The sample films were cut into circular shape with 110 mm in diameter according to ASTM 1434-82. The thickness of the films was measured with the peacock digital thickness gauge model PDN 12N by reading ten points at random position over the entire test area and the results were averaged. The films were placed in a dessicator over NaCl and kept for not less than 3 days prior to test.

Scanning electron microscopy was performed on JSM 5800 LV Model. The specimens were coated with gold under vacuum to make them electrically conductive.

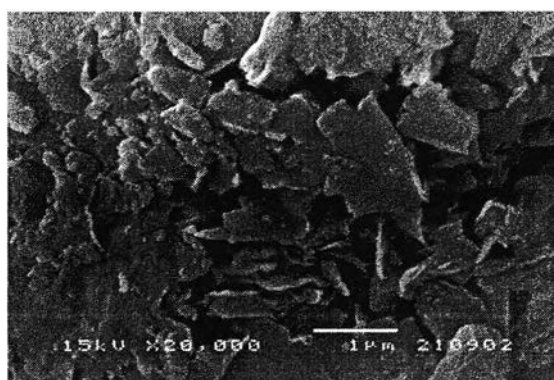
5.4 RESULTS AND DISCUSSION

Characterization of Porous Clay Heterostructures (PCHs) and Hybrid Organic-Inorganic PCHs (HPCHs)

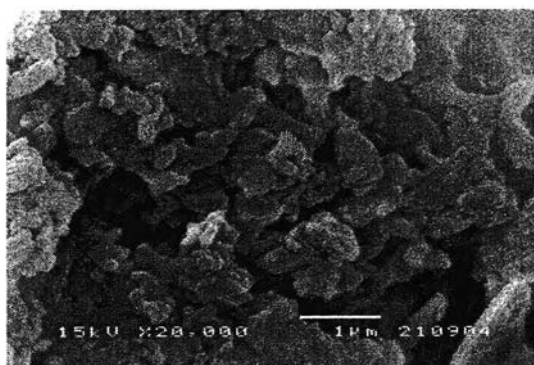
Before the synthesis of PCHs and HPCHs, pH of Na-bentonite (BTN) was adjusted and equilibrated to 9, 7, 5 and 3. After that, the PCHs and HPCHs were modified by the following step. In the first step, the gallery sodium ions in the clay host were exchanged for surfactant cetyltrimethylammonium cations. The clay layers is expanded, which facilitates the accessibility of co-surfactant (neutral amine) and silica sources (TEOS and TEOS/MTS for PCHs and HPCHs, respectively) in the second step. By solvent extraction method, the surfactant templates were removed from the as-synthesized PCHs and HPCHs, resulting in the formation of porous structures.

The BTN show a layered or plate-like structure in SEM image (Fig. 5.1(a)). After modification, the SEM images of PCH and HPCH (Fig. 5.1(b)-(c)) reveal a similar morphology to starting clay. Moreover, the presence of the clay layers can be confirmed by TEM images of both selective PCH and HPCH (Fig. 5.2(a) and (b)). From the TEM images, the clay layers are discernible as solid dark lines and reveal aggregated domains of several layers. Although the clay layers are easily observed, pore structure in the galleries of clay is more difficult to notice due to the nature of these materials. According to N_2 adsorption-desorption results in Fig. 5.3 and Table 5.1. The isotherm of BTN shows a characteristic of non-porous solid indicating low adsorption amount of nitrogen and present a plateau exactly parallel to the pressure axis while the isotherms of PCHs and HPCHs are similar. They are abruptly increase in nitrogen adsorption at low partial pressure and gradually increase to medium partial pressure (P/P_0 :0.05-0.3), suggesting that these materials possess supermicropore to small mesopore region. The BET surface area of BTN is $31 \text{ m}^2/\text{g}$. The results also reveal that the surface areas of PCHs and HPCHs increase significantly from pristine clay. Moreover, average pore diameter of both PCHs and HPCHs are in the range of 3.01-3.85 and 3.19-3.88 nm, respectively. This confirm that these materials have pore size in supermicropore to small mesopore region

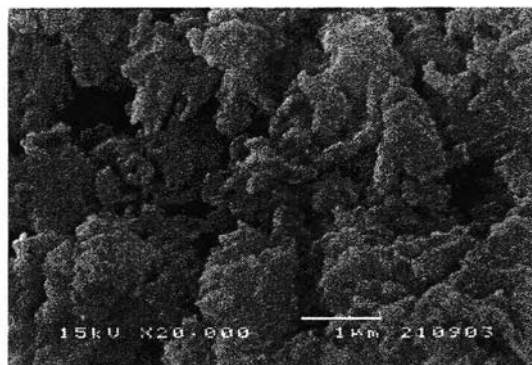
according to their characteristic isotherms. In addition, pore volume of PCHs and HPCHS is 0.43-0.64 and 0.33-0.49 cc/g, respectively. The pore volume of HPCH materials are lower than PCH materials due to the incorporation of methyl groups resulting in intensified occupation of gallery channel space.



(a)



(b)



(c)

Figure 5.1 SEM images of (a) BTN, (b) PCH-9 and (c) HPCH-9.

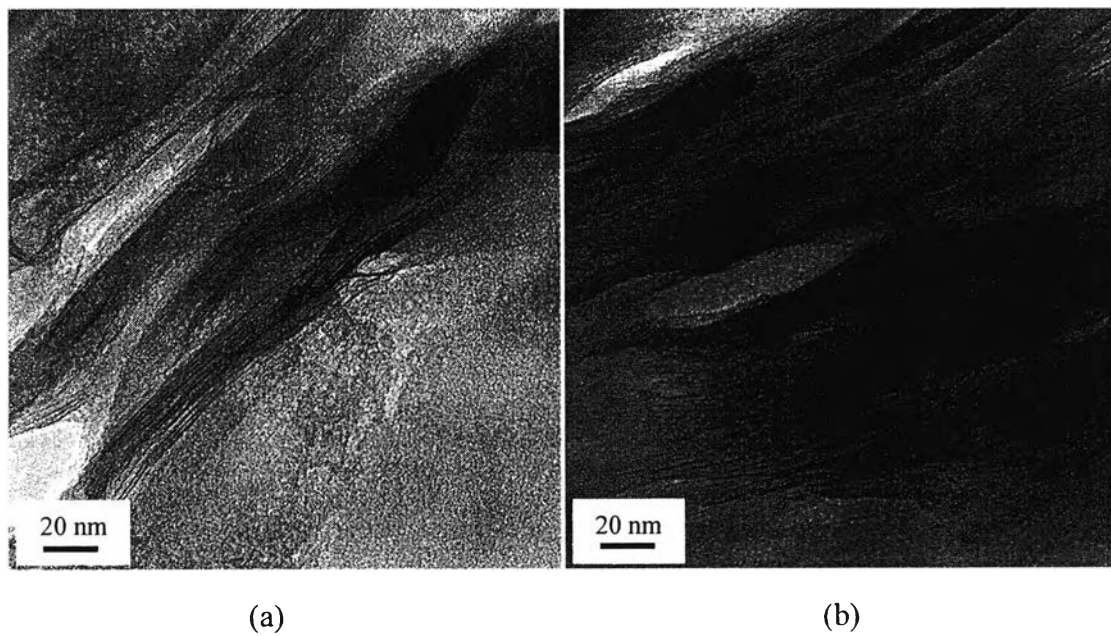


Figure 5.2 TEM images of (a) PCH-9 and (b) HPCH-9 .

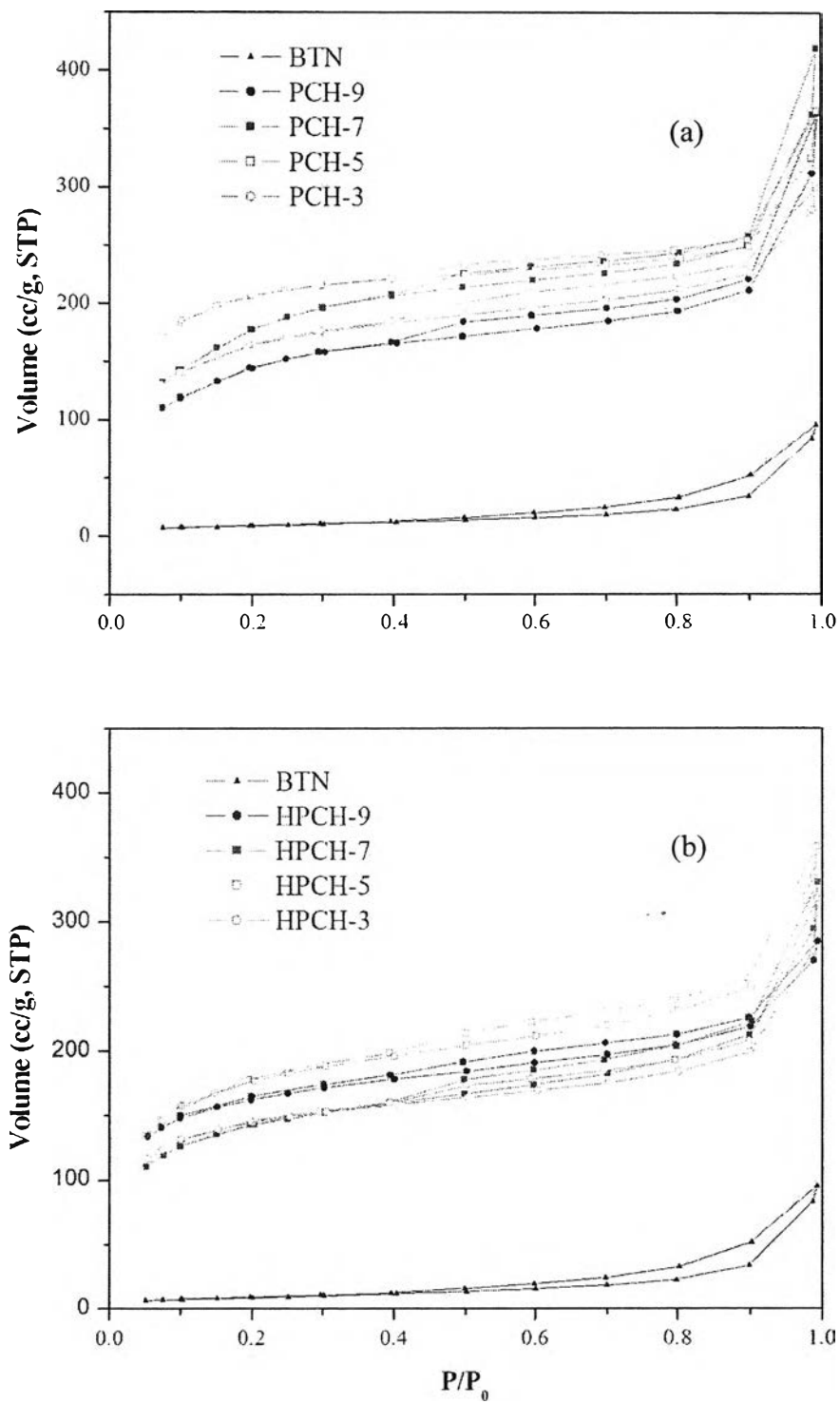


Figure 5.3 N_2 adsorption-desorption isotherms of BTN, (a) PCHs and (b) HPCHs.

Table 5.1 Porosity characteristics of BTN, PCHs and HPCHs obtained from various pH-adjusted BTN.

Sample	Multipoint BET surface area (m ² /g)	Average pore diameter (nm)	BJH pore volume (cc/g)
Bentonite	31	16.45	0.15
PCH-9	501	3.85	0.54
PCH- 7	628	3.57	0.64
PCH -5	668	3.01	0.47
PCH- 3	549	3.16	0.43
HPCH-9	469	3.88	0.45
HPCH-7	524	3.19	0.33
HPCH -5	582	3.54	0.49
HPCH 3	467	3.68	0.41

Elemental Composition of Porous Clay Nanocomposite Films

EDX analysis indicates different chemical element composition of representative porous clays nanocomposite films, which are PCH-9 and HPCH-9 nanocomposites, as presented in Table 5.2. The existence of much carbon is a normal attribute of PP matrix. SEM images and consistent EDX micrographs of the representatives are demonstrated in Fig. 5.4 and 5.5. Bentonite, which is the host clay of PCHs and HPCHs, is hydrated alumino silicates. It is comprised of a three layer structure with alumina sheets sandwiched between tetrahedral silica units. According to the EDX results, they reveal the distribution of Si, Al, and O throughout the nanocomposite films, suggesting that the porous clays could be widely dispersed on PP matrix, although their consistent SEM images exhibit clusters of the porous clays in some extent of the nanocomposites films.

Table 5.2 Element percentage of representative porous clay nanocomposite films.

Sample	Selected Chemical Element			
	C	Si	Al	O
1% PCH-9/Surlyn/PP	93.57	0.51	0.00*	5.92
1% HPCH-9/Surlyn/PP	95.07	0.60	0.12	4.20

* The value of Al is 0.00 because its amount is relatively low to C which is attributed to a polymer matrix so the value of Al will indicate with more than three decimal places.

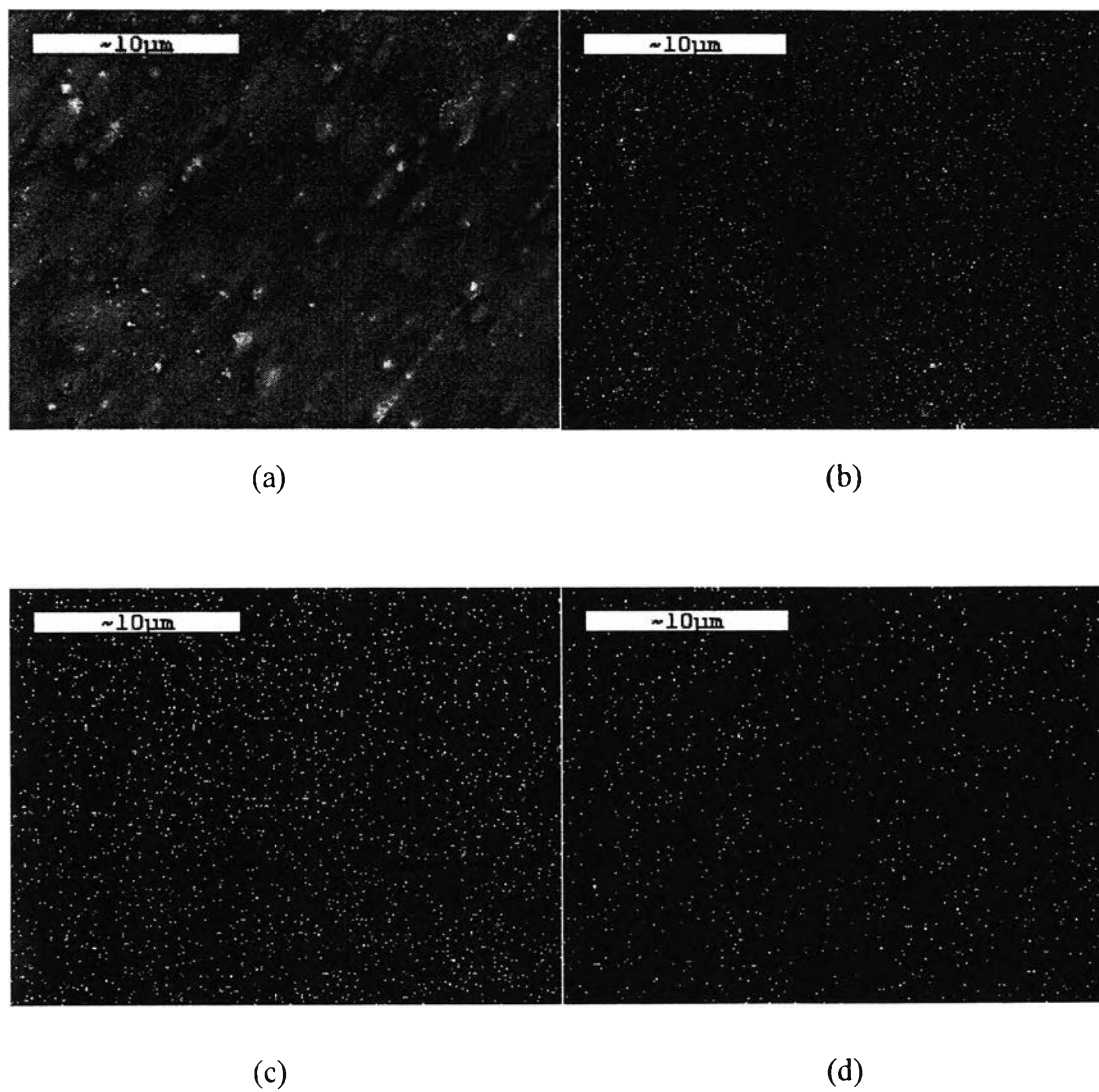


Figure 5.4 SEM image and consistent EDX micrographs of 1% PCH-9/Surlyn/PP (a) SEM image, (b) Si mapping, (c) Al mapping, and (d) O mapping.

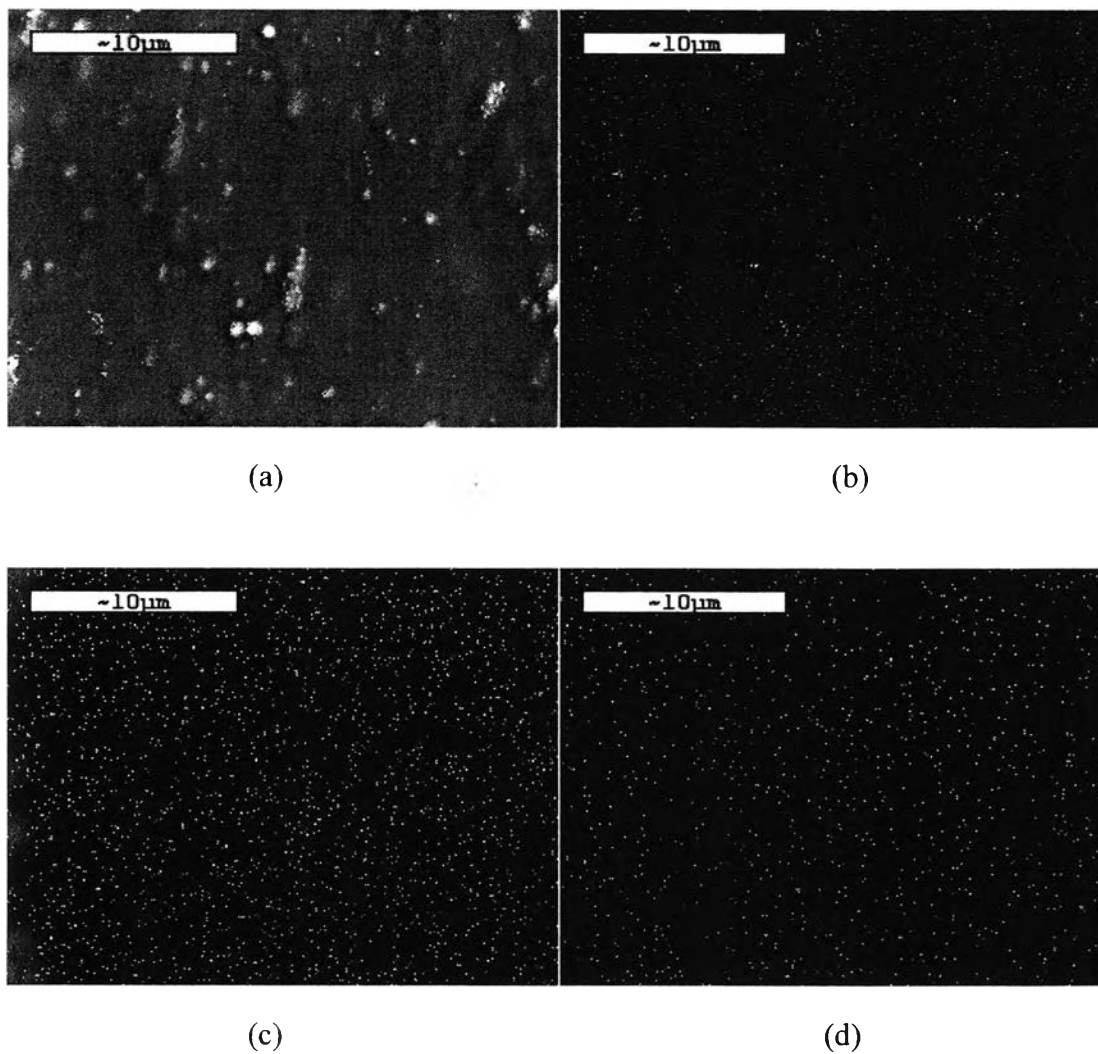


Figure 5.5 SEM image and consistent EDX micrographs of 1% HPCH-9/Surlyn/PP (a) SEM image, (b) Si mapping, (c) Al mapping, and (d) O mapping.

Crystal Structure and Crystallization Behavior of Porous Clay Nanocomposites

Crystal structure of polypropylene (PP) and porous clay nanocomposites was investigated by XRD with 2θ ranging from 2 to 40° . According to the XRD patterns, virgin PP reveals five major α -phase diffraction peaks at the following 2θ angles 14.1° , 16.9° , 18.5° , 21.0° and 21.7° from the $(110)_\alpha$, $(040)_\alpha$, $(130)_\alpha$, $(111)_\alpha$ and $(131)_\alpha$ planes, respectively [10,11], as indicated in Fig. 5.6. There is no evident difference in the XRD patterns of the porous clay nanocomposites, implying that the addition of porous clay does not affect the crystal structure of the PP matrix.

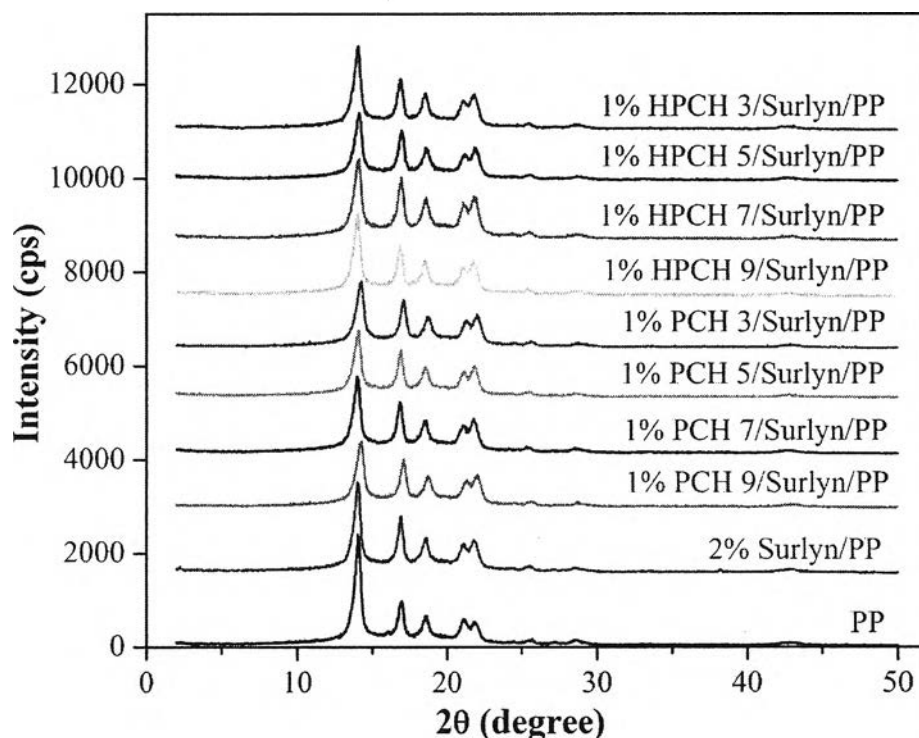


Figure 5.6 XRD patterns of PP and various porous clay nanocomposite films.

Crystallization behavior of PP and the nanocomposites are presented by DSC cooling scan thermograms in Fig. 5.7 and Table 5.3. The results show that the crystallization of PP is significantly affected by both the presence of a compatibilizer surlyn ionomer and porous clays. As shown in Fig. 5.7, the PP presents lower crystallization temperature at 110.8°C whereas the porous clay nanocomposites exhibit similar crystallization behavior to the 2% surlyn/PP, which their

crystallization peaks shift to higher temperature and stay around 115 °C. Moreover, all porous clay nanocomposites have such a higher percentage of crystallinity than that of pure PP, indicating that the PP-clay interface plays an important role in the crystallization behavior [11].

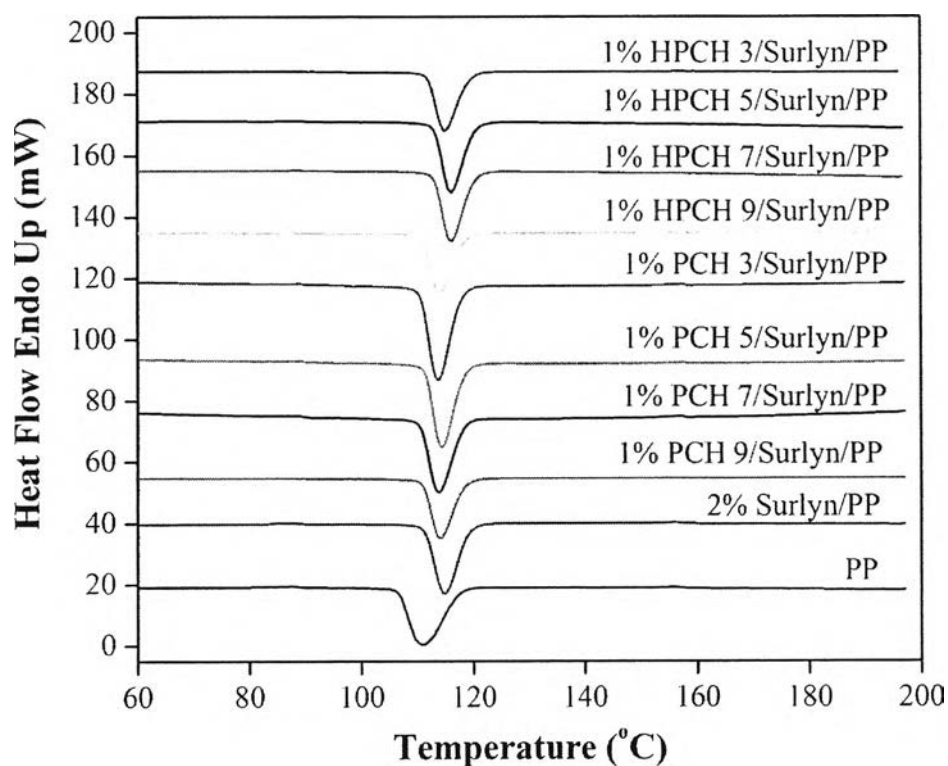


Figure 5.7 DSC cooling scan thermograms of pure PP and various porous clay nanocomposites.

Table 5.3 Crystallization behavior of PP and porous clay nanocomposites.

Sample	T _c peak (°C)	% Crystallinity
PP	110.8	37.3
2% Surlyn/PP	114.8	35.6
1% PCH 9/Surlyn/PP	114.0	46.7
1% PCH 7/Surlyn/PP	113.6	41.9
1% PCH 5/Surlyn/PP	114.3	47.7
1% PCH 3/Surlyn/PP	113.6	45.8
1% HPCH 9/Surlyn/PP	114.0	44.2
1% HPCH 7/Surlyn/PP	115.1	41.5
1% HPCH 5/Surlyn/PP	115.7	42.5
1% HPCH 3/Surlyn/PP	115.0	42.2

Thermal Properties of Porous Clay Nanocomposites

Melting temperatures of PP and the nanocomposites are observed by DSC heating scan thermograms in Fig. 5.8. The melting temperature of PP is 160.2 °C nearly the melting temperature of the porous clay nanocomposites around 162 °C. These results suggest that the additions of a compatibilizer surlyn ionomer and various types of porous clay have minimal effect on the melting temperatures. TG-DTA curves of PP and the nanocomposites are delineated in Fig. 5.9 and 5.10, and all results of thermal properties are listed in Table 5.4. The thermal degradation of PP and all nanocomposites occur in single stage, and it indicates that thermal stability of the nanocomposites are marginally increased when compared to that of virgin PP. Generally, the shift considerably towards higher temperature may be attributed to the formation of a high-performance carbonaceous-silicate char, builds up on the surface [12]. Despite all these, the results reveal that the addition of these porous materials just slightly improve the thermal stability of PP which may be responsible for some destruction of clay layers on PCHs and HPCHs materials. So they could not

dominate the thermal stability of PP. However, the residue value of char are rather consistent with the amount of clay that has been added to the PP.

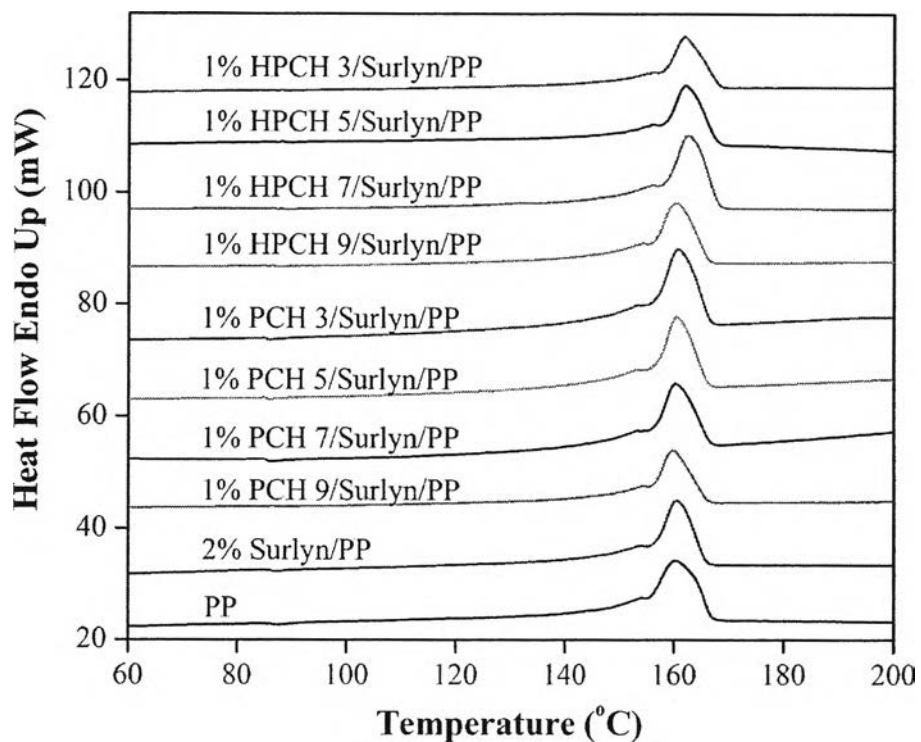


Figure 5.8 DSC heating scan thermograms of pure PP and various porous clay nanocomposites

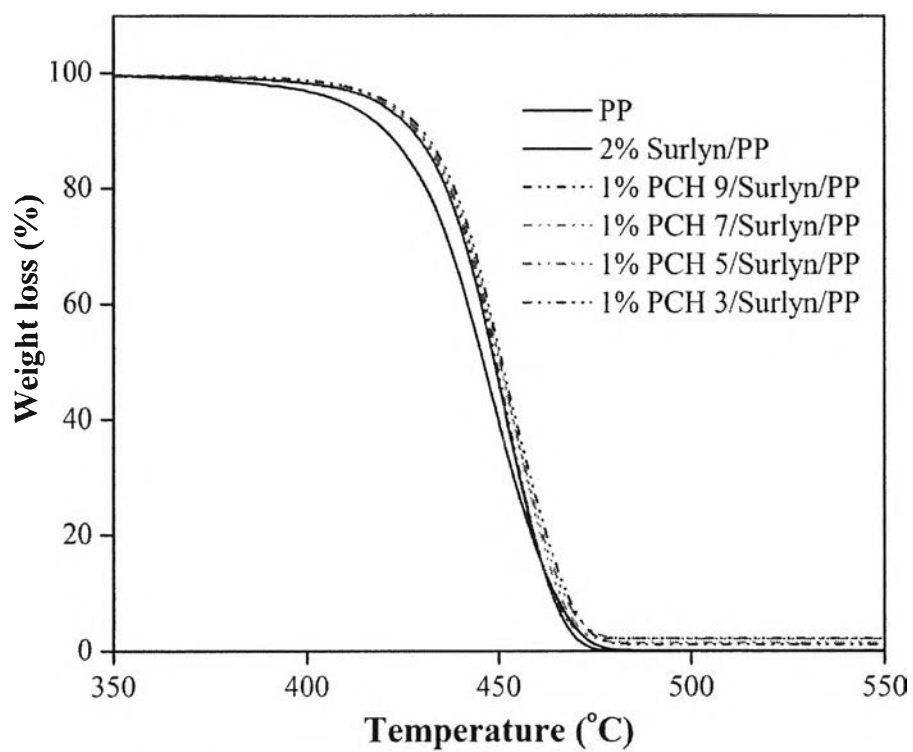


Figure 5.9 TG-DTA curves of pure PP and various PCH nanocomposites.

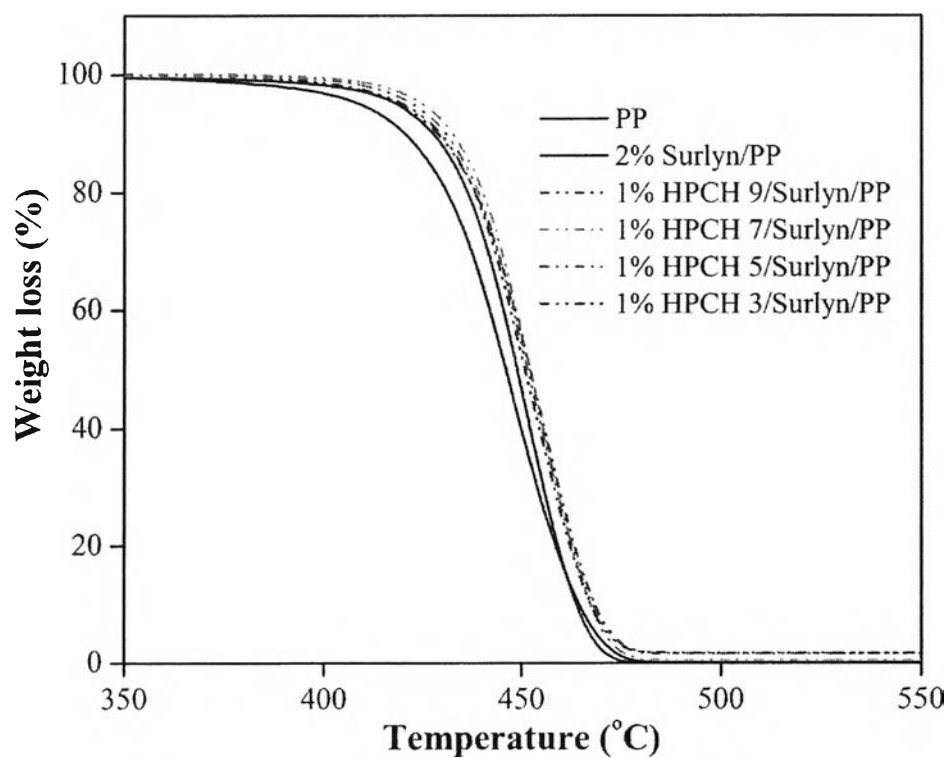


Figure 5.10 TG-DTA curves of pure PP and various HPCH nanocomposites.

Table 5.4 Thermal properties of PP and porous clay nanocomposites

Sample	T _m peak (°C)	T _d onset (°C)	Char residue at 600 °C
PP	160.2	426.4	0.1
2% Surlyn/PP	160.5	432.4	0.1
1% PCH 9/Surlyn/PP	161.4	434.4	2.3
1% PCH 7/Surlyn/PP	161.7	433.1	1.6
1% PCH 5/Surlyn/PP	162.9	432.2	2.1
1% PCH 3/Surlyn/PP	161.9	433.9	1.2
1% HPCH 9/Surlyn/PP	162.4	434.1	1.6
1% HPCH 7/Surlyn/PP	162.5	435.1	1.5
1% HPCH 5/Surlyn/PP	162.0	433.2	1.7
1% HPCH 3/Surlyn/PP	161.9	432.8	1.7

Ethylene Permeability of Porous Clay Nanocomposites

The migration of gases through materials has been a critical factor in the ability of food packaging to increase the shelf life of products. Ethylene is a plant hormone that, even in a small amount, can greatly accelerate the respiration rate of fresh fruit and thereby increase its maturation and ageing rate [13]. Generally, the presence of nanoclay (high aspect ratio) in nanocomposites provides the improvement of gas barrier properties due to the hindered diffusion pathways through the nanocomposites [14]. Ethylene permeability of PP and the porous clay nanocomposite films are summarized in Table 5.5. Both PCHs and HPCHs affect ethylene barrier property of the films, indicating by lower ethylene permeability of the nanocomposite films. Improvement in barrier property is due to the presence of PCHs and HPCHs providing tortuous path in the films owing to these materials are combined with micro- and mesoporosity so gas molecules might be induced through these porous structures. In addition, HPCHs materials could improve ethylene barrier properties than PCHs materials because the HPCHs incorporating with methyl group

have more hydrophobicity than the PCHs. So the HPCHs materials provide more interaction with ethylene gas resulting in the improvement in ethylene barrier property and also because of their pore sizes that smaller than those of PCHs materials.

Table 5.5 Ethylene permeability of PP and porous clay nanocomposite films

Sample	Ethylene permeability (ml(STP).mil/m ² .d.atm)
PP	630.60 ± 19.13
1% PCH 9/Surlyn/PP	564.39 ± 10.91
1% PCH 7/Surlyn/PP	588.81 ± 27.23
1% PCH 5/Surlyn/PP	558.85 ± 10.41
1% PCH 3/Surlyn/PP	573.21 ± 55.87
1% HPCH 9/Surlyn/PP	497.34 ± 49.73
1% HPCH 7/Surlyn/PP	530.44 ± 28.83
1% HPCH 5/Surlyn/PP	484.42 ± 65.77
1% HPCH 3/Surlyn/PP	524.67 ± 33.75

5.5 CONCLUSIONS

The modification of porous clay heterostructures (PCHs) and hybrid organic-inorganic PCHs (HPCHs) has been achieved after pH of Na-bentonite clay was adjusted to four conditions, including pH 9, 7, 5, and 3. The dispersion of the 1 wt% porous clays in PP matrix is improved by incorporating 2 wt% of surlyn ionomer. When these materials were fabricated to thin films, the effects of these porous clay on the crystal structure, crystallization behavior, thermal properties and ethylene permeability were studied. According to XRD patterns, the five characteristic peaks of PP α -phase are observed in the PP and the porous clay nanocomposites, indicating that the addition of the PCHs and HPCHs does not affect the crystal structure of PP matrix. Nevertheless, the crystallization behavior of PP is significantly affected by

both the presence of a compatibilizer surlyn ionomer and porous clays as a consequence of their crystallization peaks shift to higher temperature than that of PP. Moreover, the porous clay nanocomposites have such a higher percentage of crystallinity than that of pure PP, suggesting that the PP-clay interface plays an important role in the crystallization behavior. The additions of a compatibilizer and various types of porous clay have minimal effect on the thermal stability because the PCHs and HPCHs could not act as a mass transport barrier. According to ethylene permeability test, both PCHs and HPCHs significantly affect on the ethylene barrier property of the nanocomposite films. This points out their potential use as active packaging film for ethylene scavenger prolonging shelf-life of fruit and vegetable.

5.6 ACKNOWLEDGEMENTS

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