

Effect of Clay on Mechanical and Gas Barrier Properties of Blown Film LDPE/Clay Nanocomposites

Supong Arunvisut, Sutthipat Phummanee, Anongnat Somwangthanaroj

Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok, Thailand

Received 12 December 2006; accepted 15 May 2007

DOI 10.1002/app.26839

Published online 25 July 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Low density polyethylene (LDPE)/clay nanocomposites, which can be used in packaging industries, were prepared by melt-mix organoclay with polymer matrix (LDPE) and compatibilizer, polyethylene grafted maleic anhydride (PEMA). The pristine clay was first modified with alkylammonium salt surfactant, before melt-mixed in twin screw extruder attached to blown-film set. D-spacing of clay and thermal behavior of nanocomposites were characterized by Wide-Angle X-ray Diffraction (WAXD) and differential scanning calorimetry (DSC), respectively. WAXD pattern confirmed the increase in PEMA contents exhibited better dispersion of clay in nanocomposites. Moreover, DSC was reported the increased PEMA contents caused the decrease in degree of crystallinity. Mechanical properties of blown film specimens were

tested in two directions of tensile tests: in transverse tests (TD tests) and in machine direction tests (MD tests). Tensile modulus and tensile strength at yield were improved when clay contents increased because of the reinforcing behavior of clay on both TD and MD tests. Tensile modulus of 7 wt % of clay in nanocomposite was 100% increasing from neat LDPE in TD tests and 17% increasing in MD tests. However, elongation at yield decreased when increased in clay loading. Oxygen permeability tests of LDPE/clay nanocomposites also decreased by 24% as the clay content increased to 7 wt %. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 2210–2217, 2007

Key words: polyethylene; organoclay; films; mechanical properties; gas permeation

INTRODUCTION

Polymer/clay nanocomposites are a class of hybrid materials prepared by adding inorganic nanoparticles in an organic polymer matrix. Inorganic nanoclay, which is commonly used, is montmorillonite (MMT). MMT, which has alumino-silicate structure, consists of two tetrahedral layers sandwiching an octahedral layer and Na^+ or Ca^{2+} ions residing in the interlayer. Polymer/clay nanocomposites exhibit better mechanical,^{1–11} thermal,^{1,10–14} gas barrier,^{6,7} and other physicochemical properties^{14–16} than neat polymer. There are many interesting research reported much exfoliated clay dispersing in polymer containing a polar group^{2,3,17–19} because the polar group allowed clay to easily disperse in polymer matrix while some studies in nonpolar polymers, like polyolefin, have less degree of exfoliation of clay in polymer matrix.^{5,7,9,13–15} There are three ways to synthesize polyolefin/clay nanocomposites, i.e.,

in situ polymerization, solution method and melt mixing. From all of these, melt mixing method is the easiest and most cost effective to prepare nanocomposites. In comparison between solution and melt mixing methods, Shen et al. proposed small quantity of poly(ethylene oxide) (PEO), dissolved in a solvent showed inadequate energy to form helical structure, only formed a distorted helical structure. While more PEO chains in the system were able to form more stretch helical structure. Hence, gallery size of clay was constant when at least 20 wt % of PEO matrix was resided in the system. However, in melt mixing method, small quantity of PEO chains diffused from molten bulk polymer into silicate gallery because of thermodynamical stability of this system so the gallery size remained constant.²⁰

To melt-mix polyolefin with clay platelets, clay surface must be modified by surfactant to reduce different affinity between hydrophilic clay and hydrophobic matrix as polyolefin, called ion-exchanged reaction. To introduce ion-exchanged reaction to clay, cations in clay are replaced by alkylammonium ions in surfactant, which causes increasing interlayer spacing between clay platelets. Surfactant that is commonly used to modify clay is substances in the group of alkylammonium salt. Hotta and Paul suggested LLDPE nanocomposites using two alkyl tails as surfactant exhibited better dispersion of clay and greater improvement in their mechanical properties

Correspondence to: A. Somwangthanaroj (anongnat.s@chula.ac.th).

Contract grant sponsors: Coordinating Center for Thai Government Science and Technology Scholarship Students (CSTS), National Science and Technology Development Agency (NSTDA).

Journal of Applied Polymer Science, Vol. 106, 2210–2217 (2007)
© 2007 Wiley Periodicals, Inc.

than that using one alkyl tail surfactant because the affinity between polyolefin matrix and many alkyl tails is much better than that between polyolefin and silicate surface.⁶ Unlike LLDPE/clay nanocomposites, clay which was modified with one alkyl chain in alkylammonium salt exhibited better degree of clay dispersing in Nylon 6/clay nanocomposites than that with several alkyl chains.²¹ In addition, having long carbon atoms in alkyl chain induces much degree of exfoliation of clay in polyolefin nanocomposites. Wang and coworkers mentioned flammability properties of polyethylene (PE) nanocomposites were improved and more exfoliated clay in polymer matrix was obtained when long alkyl tail surfactant was used in organoclay.¹⁵ Besides surface modification of clay, compatibilizing agent, which is a material that composes of hydrophilic part to be compatible with clay, while the other part is hydrophobic function to blend with polymer matrix, might be considered to help synthesizing polyolefin/clay nanocomposites since it increases interfacial interaction between organophilic clay and hydrophobic polymer matrix. Ranade and coworkers reported compatibilizer helped improving mechanical properties of PE/clay nanocomposites because of a synergistic contribution of both compatibilizer and clay in nanocomposites.⁹ More degree of clay exfoliation can be obtained by mixing clay with PE grafted maleic anhydride (PEMA) when compared using neat PE as a matrix.¹³

PE film is widely used in packaging industries because of its exceptional properties, such as light weight, low cost, and easy processibility. PE blown film were produced by feeding plastic pellets into an extruder where it is melted and homogenized before it is pumped through a circular blown film die. The melt forms a continuous tube which is drawn from the die. It is inflated and simultaneously cooled by moving air. Because of a lot of consumption, clay should be filled in PE matrix to produce the materials that superior mechanical properties can be obtained. Shin et al. prepared PE/clay nanocomposites by *in situ* polymerization method, using bifunctional organic modifier. An effective exfoliation of the layered silicates, which were also chemically bonded to PE chain has been reported.²² Two equipment using for melt mixing methods were generally considered: melt mixer^{5,7,14} and screw extruder.^{16,23} Most study in PE/clay nanocomposites, injection molding or compression molding method was used to prepare specimens for mechanical and other testing.^{5-7,13,16} On the other hand, Ranade et al. used blown-film specimens to test mechanical properties.⁹ PE/clay blown-film nanocomposites interest us because a large portion of the PE produced is consumed in the film market and packaging industries.

In this study, PE/clay nanocomposites with compatibilizing agent, PEMA, were investigated in film samples using blown-film set attached to twin screw extruder for properties testing because blown-film has two different directions of fabricating force: in machine direction (MD) and in transverse direction (TD). The effect of clay on mechanical and gas barrier properties were considered in the various clay loadings. The orientation of clay platelets and the degree of crystallinity of polymer that affected the mechanical properties of nanocomposites were also discussed.

EXPERIMENTAL

Materials

Commercial grade of Low Density Polyethylene (LDPE) (El-Lene, LD1905F: MFI = 5 g/10 min and density = 0.919 g/cm³) from Cementhai Chemicals, (Thailand) and purified sodium MMT (Bentolite H: CEC = 71 meq/100 g clay) from Southern Clay Products (Gonzales, TX), were used. To prepare organoclay, MMT was mixed with Di (hydrogenated tallowalkyl) dimethyl ammonium chloride, abbreviated DHTDMAC, (Arquad 2HT-75E: 64% C₁₈ and 31% C₁₆) from Akzo Nobel Surface Chemistry PTE (Singapore). PE grafted maleic anhydride, abbreviated PEMA (Fusabond, MB100D: MFI = 2 g/10 min, density = 0.96 g/cm³ and high level of maleic anhydride) as a compatibilizing agent, was purchased from DuPont Singapore PTE (Singapore).

Modification of MMT

To prepare organoclay, MMT was combined with surfactant, called DHTDMAC. MMT (400 g) and distilled water were mixed and heated until 70°C. Then, DHTDMAC (326 g is equivalent to 1.5 CEC of MMT) was dissolved in hot mixture and stirred for 30 min. The ion exchange reaction occurred and MMT-water suspension was noticed when stirrer was stopped. The resulting white precipitate was centrifuged and dried at 70°C for 3 days or until dried. Prepared organoclay was filtered and particles smaller than 75 μm were collected.

Preparation of PE/clay nanocomposites

LDPE, PEMA and organoclay were melt-mixed by twin-screw extruder (Rheomex PTW 16/25, THERMO HAAKE, MA: L/D = 25 and D = 16 mm.) with a temperature profile of 160°C for Zones 1–4 in a extruder barrel and die zone and a screw speed of 150 rpm to obtain palletized nanocomposite from multistrand die (3-hole die). The nanocomposites were re-extruded through blown-film die with a temperature profile of 160°C for Zones 1–4 in an

TABLE I
Compositions of PE/Clay Nanocomposites Prepared

Composition (wt %)	Grade of PE/clay nanocomposites			
	PEC1	PEC3	PEC5	PEC7
Organoclay	1	3	5	7
PEMA	3	9	15	21
LDPE	96	88	80	72

extruder barrel and die zone and a screw speed of 150 rpm to fabricate film samples (50–60- μm thickness). To study effects of clay content on PE/clay nanocomposites, various clay contents were prepared. The optimum ratio of PEMA to organoclay ratio, which was kept constant for all composites at 3 : 1, was the ratio to enhance mechanical properties in preliminary study for this system (data not shown). The compositions of PE/clay nanocomposites are summarized in Table I.

Characterization

The structure of clay in PE/clay nanocomposites was characterized by Wide-Angle X-ray Diffraction (WAXD) that was performed on a D8 Advance (BRUKER, Germany) diffractometer using Cu $K\alpha$ radiation ($\lambda = 0.154 \text{ nm}$), which scanned from 1° to 10° in step size of 0.01° at a generated voltage of 40 kV and current of 40 mA at room temperature. A (001) plane indicating interlayer spacings of clay in PE/clay nanocomposite film in each samples was measured and Bragg's equation, $\lambda = 2d \sin \theta$, was used to calculate interlayer spacings of clay.

To investigate the melting behavior and the degree of crystallinity of neat PE and PE/clay nanocomposites, differential scanning calorimetry (DSC) analyses were carried out. In a Perkin Elmer Diamond DSC, around 10 mg of samples were put in aluminium pan at temperature ranges from 60 to 200°C at a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen atmosphere.

Mechanical properties of PE/clay nanocomposites

Tension tests were performed using a mechanical testing machine (INSTRON 5567) at a cross speed of 50 mm/min to measure tensile properties of neat PE and PE/clay nanocomposites. For each condition, 10 film specimens (50–60 μm thickness) were prepared according to ASTM D882-02: five specimens for transverse direction tests (TD-tests) and the remaining for machine direction tests (MD-tests).

Gas permeability test

Gas permeability tests of PE/clay nanocomposites with various clay contents were performed with an

Oxygen Permeation Analyzer (Illinois Instruments, Model 8501) according to ASTM D-3985. A blown-film of uniform thickness for each specimen (less than 2 μm variation) was mounted as a sealed semi-barrier between two chambers at ambient atmospheric pressure, 23°C in dry environment. Nitrogen gas was slowly purged in one chamber and another chamber contained oxygen gas. As oxygen gas permeated through the film into the nitrogen carrier gas, it was detected by coulometric detector. Oxygen transmission rate (OTR) was achieved as follows:

$$\text{OTR} = \frac{E_e - E_o \times Q}{A \times R_L}$$

where:

- E_e = steady-state voltage level
- E_o = zero voltage level
- A = specimen area
- Q = calibration constant
- R_L = value of load resistance

in which a computer-controlled in systems the Oxygen Permeation Analyzer automatically recorded the OTR value.

RESULTS AND DISCUSSION

Characterization

WAXD analysis is used to characterize the dispersion of clay nanoparticles in PE matrix. Figure 1 shows the WAXD patterns of nanocomposites with different clay loadings, from 1 of clay to 7 wt % of clay to compare with those of organoclay and puri-

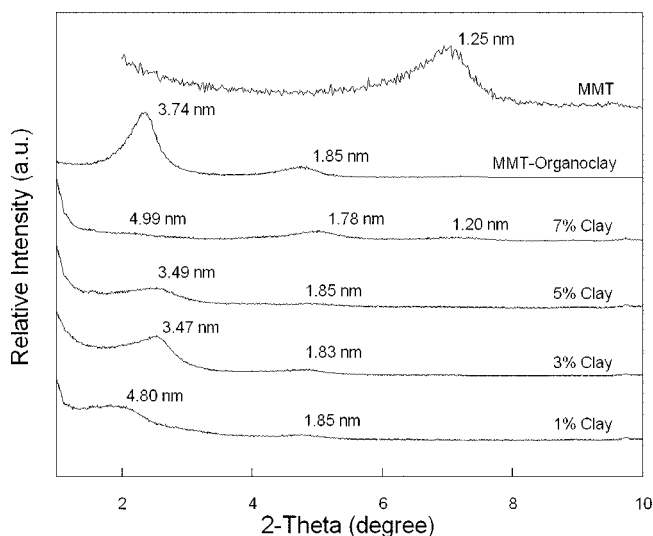


Figure 1 WAXD patterns in the range of 2θ from 1° to 10° of unmodified clay, MMT-organoclay and nanocomposites for 1, 3, 5, and 7 wt % clay.

fied clay, the angle ranges from 1° to 10° . The (001) plane of purified clay was observed approximately at $2\theta = 7.05^\circ$, equivalent to an interlayer spacing of 1.25 nm from Bragg's equation. To compare an interlayer spacing between unmodified clay and organo-clay, which was surface modified with DHTDMAC, MMT-organoclay showed an intense first peak at around $2\theta = 2.36^\circ$, corresponding to a d-spacing of 3.74 nm. The larger d-spacing of clay indicated that C_{18} molecules of two alkyl tails in the surfactant can be introduced in clay interlayer. The second peak, which occurred $\sim 2\theta = 4.76^\circ$ or equivalent to 1.85 nm, could occur due to C_{12} – C_{16} alkyl chains in the surfactant because as much as 31% C_{16} alkyl chains of quaternary ammonium ions was in the surfactant used in this study. For 1 wt % of clay in nanocomposites, broad peak was observed at around $2\theta = 1.84^\circ$, corresponding to a d-spacing of 4.80 nm. The first intense peak was shifted to lower 2θ degree on the WAXD pattern. It can be seen that a d-spacing of clay increased after mixing clay with PEMA and PE because of the intercalation of PE chains between clay platelets. Therefore, partial exfoliation of clay in 1 wt % nanocomposites occurred because some small stacks of clay platelets have left in polymer matrix. This result is consistent with Zhai et al., which reported the organoclay was intercalated in nanocomposite with small loadings of clay based on PE.¹³

Moreover, 3, 5, and 7 wt % of clay in PE nanocomposites showed the intensity of (001) plane at $2\theta = 2.53^\circ$, 2.54° , and 1.77° , respectively. From Bragg's equation, the first planes of clay were prior calculated to obtain the interlayer spacings of 3.47, 3.49, and 4.99 nm, respectively. It is noted that the peak from 3 wt % of clay in nanocomposite was observed at higher 2θ degree than from 1 wt % of clay in nanocomposite. Because there are very small amount of clay in 1 wt % sample, organoclay can be dispersed through out the polymer matrix and the interlayer spacings of clay is large. In comparison, PE/clay nanocomposite with 3 wt % of clay showed less intensity of the (001) plane than that of MMT-organoclay. The result was noticeably the intensity of the first peak of each WAXD pattern gradually decreased by increasing in clay contents. Because of the constant ratio of PEMA to clay at 3 : 1 in this system, the quantity of maleic anhydride was increasingly followed by filling higher clay content in each nanocomposite. More maleation from inserting PEMA in nanocomposites, ranged from 3 to 21 wt % of PEMA in 1–7 wt % of clay in the samples, exhibited less stack of clay platelets in nanocomposites. Chiu et al. suggested polypropylene nanocomposite with 10 wt % polypropylene-grafted maleic anhydride (PPMA) exhibited better exfoliated nanocomposites than that with 5 wt % PPMA and that with-

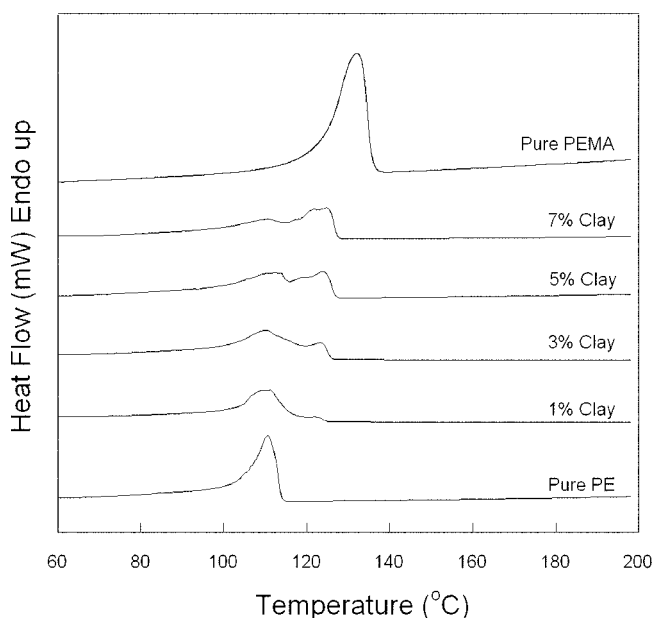


Figure 2 DSC curves in the range of temperatures from 60 to 200°C for neat PE, neat PEMA and nanocomposites for 1, 3, 5, and 7 wt % clay.

out PPMA.¹ Hotta and Paul also mentioned LLDPE/clay nanocomposites with higher amount of maleic anhydride from PEMA introduced clay to easily disperse in LLDPE matrix.⁶ Interestingly, the (001) peak nearly disappeared in the case of 7 wt % clay contents in nanocomposite. This suggests that the organoclay is well exfoliated and disordered in nanocomposites since having PEMA demonstrates clearly the influence of grafted groups of compatibilizer on the interaction between filler and polymer.¹² Also, two factors of the intercalation of clay with polymer chains in nanocomposites is explained; both maleic anhydride groups from PEMA may originate hydrogen bonds with oxygen groups of the silicates and miscibility of PEMA with PE matrix may occurred from proposed dispersion mechanism in polymer clay hybrids.²⁴

Not only the degree of clay dispersion in polymer matrix but also the thermal properties, such as melting temperature and degree of crystallinity, of nanocomposites interest us. Figure 2 shows the temperature profiles of film PE/clay nanocomposites with various clay contents from 60 to 200°C. Two peaks appeared in each curve are the melting temperature of PE and PEMA. As can be seen from the figure, the first peak at around 110°C is the melting temperature of PE and the second peak at around 125°C is the melting temperature of PEMA. For neat PEMA, the melting temperature is approximately 132°C. Increasing clay and PEMA contents, the melting temperature of PE slightly decreased but increased

in case of PEMA. These results are consistently with many works.^{1,7,9,12,25}

Furthermore, increasing clay and PEMA contents significantly reduced the melting enthalpies of PE but increased those of PEMA; in case of 7 wt % of clay nanocomposite, the melting enthalpies of PE reduced by 90% compared with pristine PE, while the melting enthalpies of PEMA in that nanocomposite reduced only by 18%. To consider the melting enthalpies of nanocomposites, these tend to decrease when nanocomposites had large amount of clay and PEMA. Increasing in clay contents by kept constant PEMA content in nanocomposites, the melting enthalpies of nanocomposites reduced but increased in case of increasing in PEMA by steady clay loadings. Interestingly, the presence of PEMA and clay together in nanocomposites can reduced the melting enthalpies of the nanocomposites.⁹ Morawiec et al. also observed the effect of PEMA and clay with various contents to the melting enthalpies of nanocomposites by fixed the ratio of PEMA:clay as 2 : 1.¹² These results consistence with our study and it can be described that the presence of both large amount of maleic anhydride groups and organoclay in the nanocomposites decrease melting enthalpies. Finally, these results refer that the nanocomposites have less degree of crystallinity.^{7,12,26} The results are summarized in Table II.

Mechanical properties

The mechanical properties was measured for film (50–60 μm in thickness) using INSTRON machine at a cross speed of 50 mm/min. Ten specimens were prepared for each sample; five pieces for TD tests and the remaining for MD tests. To compare 7 wt % clay nanocomposite with neat PE in two different direction tests (TD and MD tests), typical stress–strain diagrams are shown in Figures 3 and 4, respectively. The tensile modulus was computed from each such plot as the tangent of the initial part of the stress–strain curve. For TD tests, adding 7 wt % of clay in PE nanocomposite improved in tensile strength at yield and tensile modulus significantly. For this point, filling only small contents of nanopar-

TABLE II
DSC Results of PE/Clay Nanocomposites

Composition (wt %)	T_m ($^{\circ}\text{C}$)		H_m (J/g)		
	LDPE	PEMA	LDPE	PEMA	Nanocomposite
LDPE	110.6	–	92.5	–	–
PEC1	111.3	122.7	65.8	36.8	64.4
PEC3	110.7	123.7	37.8	72.6	40.3
PEC5	110.4	124.2	20.7	129.5	37.0
PEC7	110.3	125.1	9.5	132.1	35.1
PEMA	–	132.9	–	156.5	–

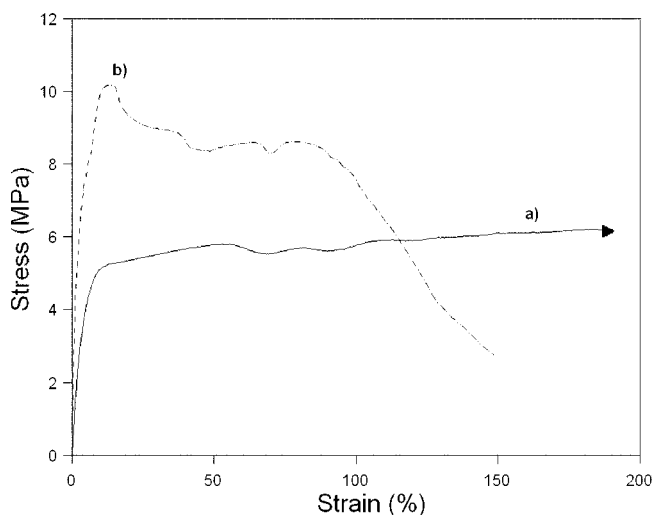


Figure 3 Stress–strain diagrams of (a) neat PE and (b) 7 wt % of clay in PE/clay nanocomposite for TD tests.

ticle clay in polymer matrix exhibited better mechanical properties than conventional composites, which were due to the large surface area of nanoparticles, which induced the enormous interfacial interaction between nanoparticle and polymer matrix.^{27,28} Cho and Paul reported Nylon 6/clay nanocomposites were clearly shown better mechanical properties than Nylon 6/fiber composites.² For MD tests, however, the mechanical properties of PE/clay nanocomposites slightly improved when polymer matrix was added with 7 wt % of clay.

Figures 5 and 6 show tensile modulus and yield strength of LDPE nanocomposites, respectively, for various clay contents and two different direction tests. The trends in modulus and yield strength of LDPE/clay nanocomposites was plotted as a function of clay loading and types of tension, transverse

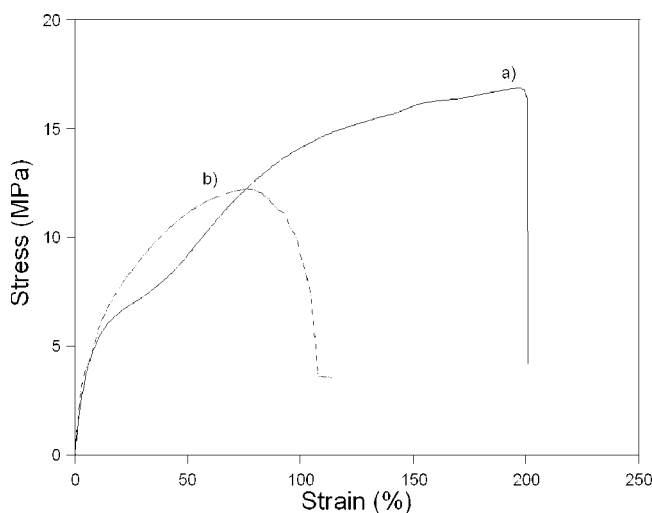


Figure 4 Stress–strain diagrams of (a) neat PE and (b) 7 wt % of clay in PE/clay nanocomposite for MD tests.

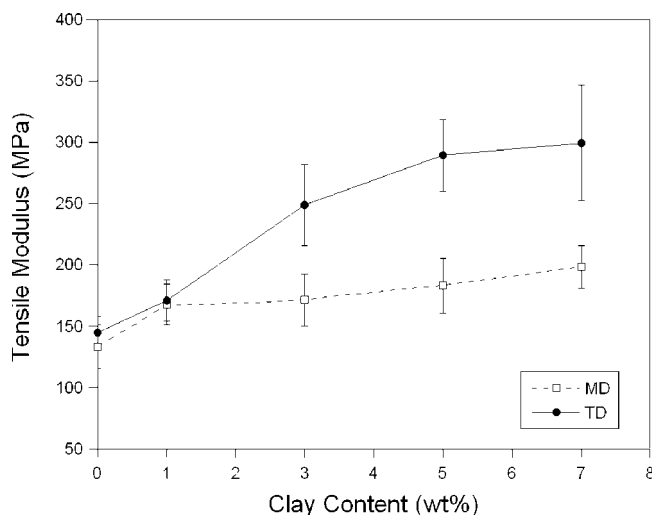


Figure 5 Effect of clay content and the direction of tensile tests on tensile modulus for TD tests (●) and MD tests (□).

and MD. In Figure 5, it is shown that when clay contents increased, tensile modulus increased in both machine and TDs. For TD tests, tensile modulus increased significantly, from 145 to 290 MPa, between 0 wt % clay (neat PE) and 5 wt % clay nanocomposites, which is an increase by 100% in tensile modulus of TD when compare with neat PE, after that, there was a slight increase in tensile modulus in the case of 7 wt % of clay in nanocomposite. However, for MD tests, modulus increased gradually around 30% of neat PE in the case of 1 wt % of clay. Then, there was a slight increase by 17% from 1 wt % of clay to 7 wt % of clay ranged from 170 to 200 MPa, respectively. The tensile modulus enhancement of nanocomposite film in TD direction was due to both polymer chain orientation^{27,29} and nanoparticle orientation.²⁷ The polymer chain orientation in TD direction was caused by an expansion of the bubble in the hoop direction, in which the good correlation between mechanical properties enhancement and orientation anisotropy was found.²⁹

In the case of tensile strength at yield, for MD tests, PE/clay nanocomposite was improved by 25% with adding 3 wt % in clay content compare with neat PE in Figure 6; 6 MPa value of tensile strength for neat PE went up considerably to 7.5 MPa for the clay loadings of 3 wt % in nanocomposites and then yield strength remained constant until 7 wt % in clay loading. However, related to neat PE, there was a drop in tensile strength at yield of TD tests with filling 1 wt % of clay since the presence of maleic anhydride in material cause two effects in properties of nanocomposites. Firstly, PEMA is an oligomer whose molecular weight is lower than LDPE and its mechanical properties is also lower than that of neat LDPE. Moreover, due to melt-mix of nanocomposites

at high temperature, in 140°C, PEMA caused LDPE chain scission into lower molecular weight³⁰ which was confirmed by its rheological properties.³¹ As a result, there are a number of low molecular weight molecules in the mixture and mechanical properties can be reduced when nanocomposites have much more low molecular weight chains.³ Interestingly, yield strength increased dramatically by 100% going up from 5.0 MPa for 1 wt % of clay to 10.1 MPa for 7 wt % of clay. Although, the presence of PEMA causes scissoring of LDPE chains, the presence of more clay contents, from 1 to 7 wt % of clay in nanocomposites affects the enhancement of mechanical properties so it can be said that clay behave reinforcing filler in nanocomposites.

In spite of the result of previous section, the decrease in degree of crystallinity of polymer dropped in mechanical properties in blending PE and PEMA,⁶ the presence of clay in nanocomposites develop mechanical properties, such as tensile modulus and tensile strength at yield. In comparison, Lopez et al. reported 7 wt % of clay in PP nanocomposites have more tensile modulus than neat PP, by 42%, going up from 1.8 to 2.6 GPa.⁴ Moreover, WAXD pattern of the nanocomposite was indicated the inadequate intercalation of clay with polypropylene chains because the first intense peak of the nanocomposite was significantly observed. These results can be confirmed that clay has reinforcing behavior to strengthen polymer matrix. Furthermore, more degree of exfoliation of clay in nanocomposites affects mechanical properties. In case of increased clay contents, tensile modulus and tensile strength consistently increase for many works.^{5-9,16}

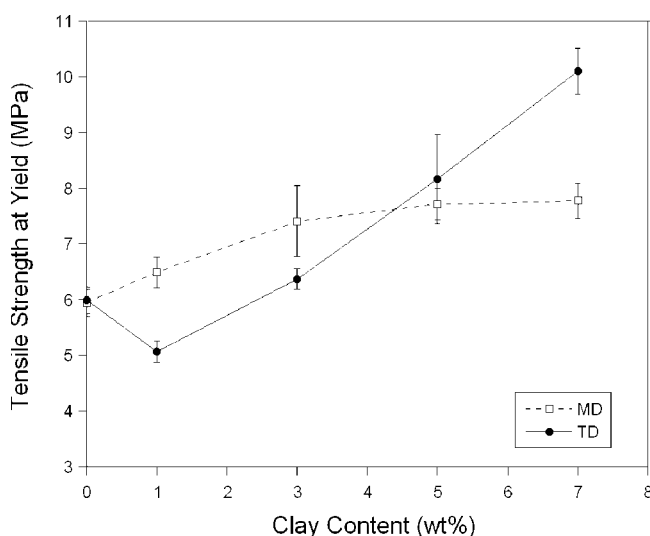


Figure 6 Effect of clay content and the direction of tensile tests on tensile strength at yield for TD tests (●) and MD tests (□).

In Figure 7, elongation at yield of PE/clay nanocomposites decreased in the case of increasing in clay contents for both directions; for TD tests, elongation at yield fell significantly from 56% elongation for neat LDPE to about 20% elongation in the case of 1 wt % of clay contents, decreasing by 82%. Next, there was a gradual drop to 10% elongation in 3 wt % of clay loadings and then it remains steady until 7 wt % of clay in PE/clay nanocomposites. In addition, there was a slight decrease by 53% in MD tests between neat LDPE and 7 wt % of clay in nanocomposites, from 15 to 7% in elongation. In general, elongation of nanocomposites decreased due to increasing the amount of clay.^{3,6,7,19,32} Although, the presence of clay in nanocomposites causes decrease in elongation, adding compatibilizer in nanocomposites, called compatibilized nanocomposites, exhibits plastically drawability with the same clay content.¹²

Gas permeability

Figure 8 shows gas permeability of LDPE and LDPE/clay nanocomposites film for O₂ gas. When clay contents were increased in PE/clay nanocomposites, from neat PE to 7 wt % of clay, oxygen permeability slightly decreased by 24%; from 3.8×10^{-6} cc m/s atm m² for neat LDPE to 2.9×10^{-6} cc m/s atm m² for 7 wt % of clay in PE/clay nanocomposites. As a result, the orientation of clay in PE/clay nanocomposites affects less gas permeability than neat PE. Moreover, disordered dispersion of clay platelets causes more difficult gas barrier through PE/clay nanocomposites. Hence, introducing nano-clay into LDPE improved the gas barrier property.

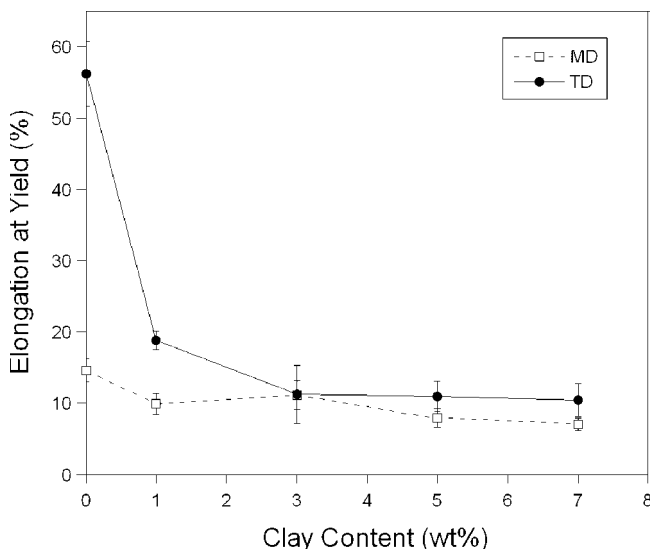


Figure 7 Effect of clay content and the direction of tensile tests on elongation at yield for TD tests (●) and MD tests (□).

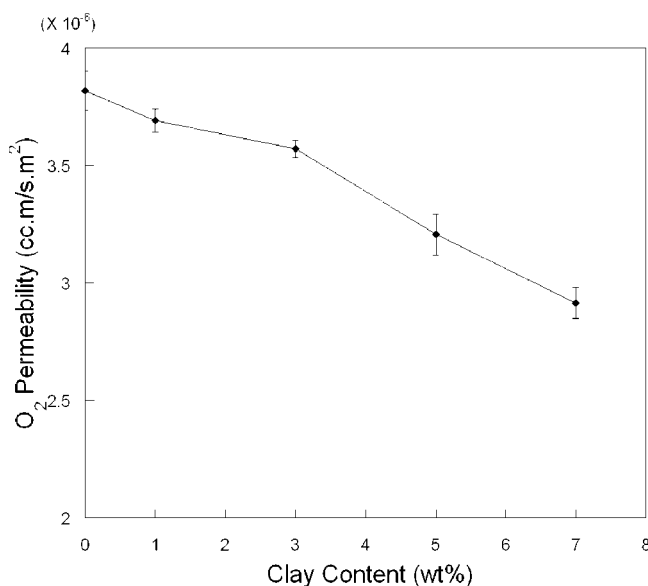


Figure 8 Gas permeability of LDPE and LDPE/clay nanocomposites for 1, 3, 5, and 7 wt % clay.

Hotta and Paul reported gas permeability also improved when clay contents were increased and TEM analysis supported the degree of clay platelet alignment affected to gas permeability.⁶ Also, Lee et al. confirmed N₂ and CO₂ permeability could be decreased with increasing clay content because of the tortuous path constructed by clay platelet.⁷

CONCLUSION

The presence of PEMA caused better degree of dispersion of clay in LDPE/clay nanocomposites, which could be due to both hydrogen bonding between maleic anhydride groups from PEMA and oxygen groups in silicate layers and miscibility of PEMA on PE. More maleic anhydride groups from PEMA exhibited better degree of exfoliation of clay and less stacks of clay platelets in nanocomposites. However, melting temperature of materials decreased slightly and degree of crystallinity in nanocomposites also dropped when clay contents increased. Nevertheless, tensile modulus and tensile strength at yield of blown film LDPE/clay nanocomposites improved in both TD and MD tests when compared between 7 wt % PE/clay nanocomposites and neat PE; tensile modulus increased by 100% for TD tests and 17% for MD tests, while yield strength increased by 100% for TD tests and 25% for MD tests. These results showed clay behaved as reinforcing filler in these materials. Also, better dispersion of clay in nanocomposites improved mechanical properties. Finally, more quantity of clay in PE/clay nanocomposites improved gas barrier properties because the disordered clay in

nanocomposites hindered oxygen permeability in nanocomposites.

Preparation of organoclay, was carried out in Metallurgy and Material Science Research and Institute (MMRI). LDPE, as a polymer matrix, was supported by Cementhai Chemicals Co., Ltd. We would like to thank Center for Nanoscience and Nanotechnology (Mahidol University, Bangkok, Thailand) for measurement of WAXD.

References

1. Chiu, F. C.; Lai, S. M.; Chenand, J. W.; Chu, P. H. *J Polym Sci Part B: Polym Phys* 2004, 42, 4139.
2. Choand, J. W.; Paul, D. R. *Polymer* 2001, 42, 1083.
3. Fornes, T. D.; Yoon, P. J.; Keskkulaand, H.; Paul, D. R. *Polymer* 2001, 42, 9929.
4. Garcia-Lopez, D.; Picazo, O.; Merinoand, J. C.; Pastor, J. M. *Eur Polym J* 2003, 39, 945.
5. Gopakumar, T. G.; Lee, J. A.; Kontopoulouand, M.; Parent, J. S. *Polymer* 2002, 43, 5483.
6. Hottaand, S.; Paul, D. R. *Polymer* 2004, 45, 7639.
7. Lee, J. H.; Jung, D.; Hong, C. E.; Rheeand, K. Y.; Advani, S. G. *Compos Sci Technol* 2005, 65, 1996.
8. Liuand, X. H.; Wu, Q. J. *Polymer* 2001, 42, 10013.
9. Ranade, A.; Nayak, K.; Fairbrotherand, D.; D'Souza, N. A. *Polymer* 2005, 46, 7323.
10. Burmistr, M. V.; Sukhyy, K. M.; Shilov, V. V.; Pissis, P.; Spanoudaki, A.; Sukha, I. V.; Tomiloand, V. I.; Gomza, Y. P. *Polymer* 2005, 46, 12226.
11. Hambir, S.; Bulakhand, N.; Jog, J. P. *Polym Eng Sci* 2002, 42, 1800.
12. Morawiec, J.; Pawlak, A.; Slouf, M.; Galeski, A.; Piorowskaand, E.; Krasnikowa, N. *Eur Polym J* 2005, 41, 1115.
13. Zhai, H. B.; Xu, W. B.; Guo, H. Y.; Zhou, Z. F.; Shenand, S. J.; Song, Q. S. *Eur Polym J* 2004, 40, 2539.
14. Zhangand, J. G.; Wilkie, C. A. *Polym Degrad Stab* 2003, 80, 163.
15. Wang, S. F.; Hu, Y.; Qu, Z. K.; Wang, Z. Z.; Chenand, Z. Y.; Fan, W. C. *Mater Lett* 2003, 57, 2675.
16. Zhao, C. G.; Qin, H. L.; Gong, F. L.; Feng, M.; Zhangand, S. M.; Yang, M. S. *Polym Degrad Stab* 2005, 87, 183.
17. Liang, Z. M.; Yinand, H.; Xu, H. H. *Polymer* 2003, 44, 1391.
18. Yu, Y. H.; Lin, C. Y.; Yehand, J. M.; Lin, W. H. *Polymer* 2003, 44, 3553.
19. Park, C.; Smith, J. G.; Connell, J. W.; Lowther, S. E.; Workin-gand, D. C.; Siochi, E. J. *Polymer* 2005, 46, 9694.
20. Shen, Z. Q.; Simonand, G. P.; Cheng, Y. B. *Polymer* 2002, 43, 4251.
21. Fornes, T. D.; Hunterand, D. L.; Paul, D. R. *Macromolecules* 2004, 37, 1793.
22. Shin, S. Y. A.; Simon, L. C.; Soaresand, J. B. P.; Scholz, G. *Polymer* 2003, 44, 5317.
23. Wang, K. H.; Choi, M. H.; Koo, C. M.; Choiand, Y. S.; Chung, I. J. *Polymer* 2001, 42, 9819.
24. Kawasumi, M.; Hasegawa, N.; Kato, M.; Usukiand, A.; Okada, A. *Macromolecules* 1997, 30, 6333.
25. Zhang, Y. Q.; Lee, J. H.; Jangand, H. J.; Nah, C. W. *Compos B* 2004, 35, 133.
26. Kim, Y. C. *Polym J* 2006, 38, 250.
27. Diramaand, T.; Goettler, L. A. *Mater Manufact Processes* 2006, 21, 199.
28. Giannelis, E. P. *Adv Mater* 1996, 8, 29.
29. Chen, H. Y.; Bishop, M. T.; Landesand, B. G.; Chum, S. P. *J Appl Polym Sci* 2006, 101, 898.
30. Ho, R. M.; Su, A. C.; Wuand, C. H.; Chen, S. I. *Polymer* 1993, 34, 3264.
31. Solomon, M. J.; Almusallam, A. S.; Seefeldt, K. F.; Somwangth-anarojand, A.; Varadan, P. *Macromolecules* 2001, 34, 1864.
32. Bergaya, F.; Mandaliaand, T.; Amigouet, P. *Colloid Polym Sci* 2005, 283, 773.