

Influence of Nanoclay on Properties of HDPE/Wood Composites

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ABSTRACT: Composites based on high density polyethylene (HDPE), pine flour, and organic clay were made by melt compounding and then injection molding. The influence of clay on crystallization behavior, mechanical properties, water absorption, and thermal stability of HDPE/pine composites was investigated. The HDPE/pine composites containing exfoliated clay were made by a two-step melt compounding procedure with the aid of a maleated polyethylene (MAPE). The use of 2% clay decreased the crystallization temperature (T_c), crystallization rate, and the crystallinity level of the HDPE/pine composites, but did not change the crystalline thickness. When 2% MAPE was added, the crystallization rate increased, but the crystallinity level was further lowered. The flexural and tensile strength of HDPE/

pine composites increased about 20 and 24%, respectively, with addition of 1% clay, but then decreased slightly as the clay content increased to 3%. The tensile modulus and tensile elongation were also increased with the addition of 1% clay. The impact strength was lowered about 7% by 1% clay, but did not decrease further as more clay was added. The MAPE improved the state of dispersion in the composites. Moisture content and thickness swelling of the HDPE/pine composites was reduced by the clay, but the clay did not improve the composite thermal stability. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 3958–3966, 2007

Key words: clay; composites; polyethylene; crystallization; wood

INTRODUCTION

Global ecological concern has resulted in a renewed interest in natural materials. Natural organic fibers from renewable natural resources offer the potential to act as biodegradable reinforcing materials alternative for the use of glass or carbon fiber and inorganic fillers. The fibers have several advantages, such as their high specific strength and modulus, low cost, low density, renewable nature, absence of associated health hazards, easy fiber surface modification, wide availability, and relative nonabrasiveness.^{1–3}

Much work has been done in studying and developing thermoplastic/natural fibers composites, especially wood plastic composites, which have successfully proven their high qualities in various fields of technical application, especially in load-bearing applications. Thermoplastics, such as polyethylene (PE),^{4–8} polypropylene (PP),^{9–11} poly(vinyl chloride),^{12,13} polystyrene,¹⁴ and poly(lactic acid) (PLA)^{15,16} have been

compounded with natural fibers (such as fibers from wood, kenaf, flax, hemp, cotton, Kraft pulp, coconut husk, areca fruit, pineapple leaf, oil palm, sisal, jute, etc.) to prepare composites. However, much of the commercial use of natural fibers in the United States in plastics has been limited to wood flour. Using wood flour as filler in these composites increases stiffness, but also reduces toughness.⁸ Creation of stress concentrations at fiber ends and poor interfacial adhesion between wood and synthetic polymer have been recognized as the leading causes for the brittleness of these composites. Much of the work in this field focuses on developing new coupling agents and compatibilizers,^{17–21} as well as improving processing methods.^{22,23}

Impressive enhancement of material properties achieved with the inclusion of submicron-size fillers in plastics and elastomers has stimulated active research. Clay nanocomposites, especially nanoclay/polymer composites, exhibit dramatic increases in modulus, strength, barrier properties, flammability resistance, and heat resistance compared with conventional composites.^{24–30} Because PE is hydrophobic and has poor miscibility with hydrophilic clay silicates, PE/clay hybrids are not easily prepared. In general, the clay is modified with alkylammonium groups to facilitate its interaction with PE, and the miscibility of PE with clay can be enhanced by intro-

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ducing compatibilizers containing polar groups, such as maleated polyethylene (MAPE), carboxylated PE, etc.^{31–38}

Wang et al.³³ reported the exfoliation and intercalation behaviors of MAPE/clay nanocomposites prepared by simple melt compounding, and they concluded that exfoliation and intercalation behaviors were dependent on the MAPE content and the chain length of organic modifier in the clay. Koo et al.³⁴ reported that the final morphology and the anisotropic phase formation of MAPE/layered silicate nanocomposites depend on the clay content. With the aid of MAPE, Kato et al.³⁵ prepared PE/clay hybrids that exhibit higher tensile yield strengths and tensile moduli than those of PE matrices and those of PE/inorganic clay composites. The gas permeability of the PE/MAPE blend decreased 30% when clay was added. Lee et al.³⁶ reported that the peak temperature of crystallization, the crystallinity, and the thermal conductivity of the nanocomposites decreased with an increase of the silicate volume fraction. It was also reported that the dispersed clay layers effectively acted a nucleating agent, resulting in the increase of crystallization peak temperature of PE.^{37,38}

However, little effort has been made to improve the properties of PE/wood composites with nanoclay. The objectives are to: (1) prepare HDPE/pine composites containing exfoliated nanoclay and (2) study the effect of clay on the crystallization, crystallinity, and mechanical properties, as well as the moisture and thermal stability of HDPE/wood composites.

EXPERIMENTAL

Materials

High density polyethylene (grade HD6605) with a melt index of 5 g/10 min (190°C, 2.16 kg) and a density of 0.948 g/cm³ was obtained from ExxonMobil Chemical. Cloisite[®] (Houston, TX) 15A, a natural montmorillonite modified with a dimethyl-dihydrogenated tallow-ammonium chloride, was obtained from Southern Clay Products, Inc. (Gonzales, TX). Less than 10% of the dry clay particles are greater than 13 μm in diameter. A MAPE compatibilizer (Polybond[®] 3009) with a melt index of 5 g/10 min (190°C, 2.16 kg) and 1.0 wt % maleic anhydride was obtained from Chemtura Corporation (Middlebury, CT). Pine (*Pinus* sp.) flour with a nominal 20-mesh particle size from American Wood Fibers (Schofield, WI) was used in the experiment.

Preparation of HDPE/pine/clay composites

A 1-L thermokinetic high-shear mixer (i.e., K-mixer from Synergistics Industries) was used to blend the composites. The raw materials were compounded in

the K-mixer at 5000 rpm and discharged when a temperature of 190°C was reached. The blending was completed in one step for all systems except for the one containing both clay and MAPE, in which a MAPE/clay masterbatch was first made by melt-blending MAPE with the clay in the K-mixer with a screw speed of 5000 rpm until the temperature reached 200°C. The masterbatch was then compounded with other materials in second step to achieve targeted formulations. Based on the HDPE weight, the loading level of clay varied from 1 to 3%. The loading levels of pine flour and MAPE were fixed at 30 and 2% based on the total weight of HDPE and pine flour. HDPE/clay and HDPE/pine blends were also made as controls.

The blends were granulated to pass a 1-cm opening screen with 1 cm in diameter, using a granulator (BP68scs from Ball and Jewel). The milled material was then injection molded at 199°C with a screw speed of 200 rpm and a mold temperature of 100°C, using a 33-ton reciprocating-screw injection molder (Vista Sentry VSX from Cincinnati Milacron).

Measurements

Wide angle X-ray diffraction (XRD) analysis was carried out to investigate the effectiveness of the clay intercalation and the change of crystalline thickness of HDPE in the composite. XRD samples were taken from injection molded specimens and were mounted to the XRD platform for analysis. To study the effect of wood and bagasse fiber on the XRD results of the composites, both loose fiber (20 mesh) and fiber mat compressed at 30 ton pressure to form a plate shape were analyzed. A 2θ range from 2° to 40° in reflection mode was scanned at 2°/min. A computer-controlled wide angle goniometer coupled to a sealed-tube source of Cu K_α radiation ($\lambda = 1.54056 \text{ \AA}$) was used. The Cu K_α line was filtered electronically with a thin Ni filter. The interlayer distance of the clay in the hybrids was calculated from the (001) lattice plane diffraction peak using Bragg's equation, and the PE crystalline thickness perpendicular to the reflection plane was obtained according to Scherrer's equation with the instrument width of 0.16°.

The crystallization behavior of HDPE in the hybrids was measured using a differential scanning calorimeter (TA DSC Q100). Samples of 4–5 mg were placed in aluminum capsules and heated from 40 to 160°C at 10°C/min to eliminate the heat history before cooling at 10°C/min. The heat flow rate corresponding to the crystallization of HDPE in composites was corrected for the content of wood fiber and MAPE. The value of crystallization heat was also corrected for the crystallization heat of MAPE.

Thermogravimetric analysis was employed to observe the thermal character of hybrids with a TA

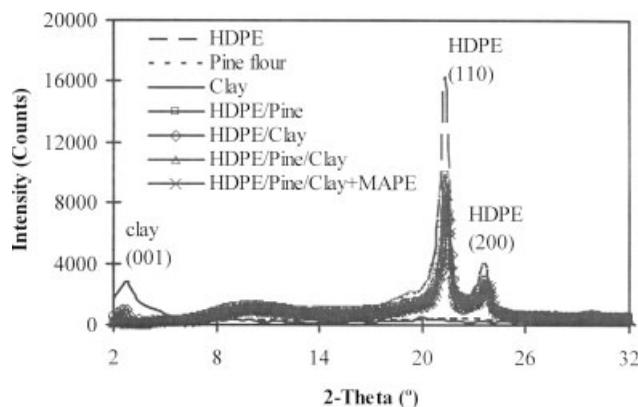


Figure 1 XRD patterns of the clay, HDPE, wood, and HDPE composites at $2^\circ/\text{min}$ for 2θ angles of 2° – 32° . The weight ratio of HDPE and pine in the composites containing pine was 70 : 30; MAPE concentration was 2% based on the total weight of HDPE and pine; clay content was 2% based on the HDPE weight. The same applies to other figures shown in this article.

Q50 Thermogravimetric Analyzer under nitrogen at a scan rate of $10^\circ\text{C}/\text{min}$ from room temperature to 650°C . A Sample of 6–8 mg was used for each run.

The flexural strength and tensile strength were measured according to the ASTM D790-03 and D638-03, respectively, using an INSTRON machine (Model 1125, Boston, MA). For each treatment level, five replications were tested. A TINIUS 92T impact tester (Testing Machine, Horsham, PA) was used for the Izod impact test. All samples were notched at the center point of one longitudinal side according to the ASTM D256. For each treatment level, five replications were tested. Statistical analysis (i.e., Duncan's multiple range test) was done to test difference of various properties at different treatment levels.

Water absorption and swelling tests were done through two steps. After conditioning the samples at 80°C to a constant weight, they were held under vacuum for 30 min at -1.0×10^4 Pa pressure, and then impregnated with water. The impregnated samples were then completely submerged in water at room temperature. At 10-day intervals, the samples were taken out, then weighed and measured for their dimensions after the surface water was removed. Three and nine replicates were measured to determine weight and thickness, respectively.

RESULTS AND DISCUSSION

Dispersion behavior of clay

The XRD patterns of the clay, wood, HDPE and its composites in the 2θ range of 2° – 32° spectrum are shown in Figure 1. The peaks appearing at 2° – 3° correspond to clay, and the strong peaks appearing at about 21.3° and 23.6° are from the (110) lattice plane and (200) lattice plane of HDPE crystals, respec-

tively. Figure 2(a,b) show the measured intensity data over the characteristic 2θ range for clay, and RHDPE and wood, respectively. As shown in Figure 2a, a strong peak was present at the position of 2.75° for clay, which corresponds to a d -spacing of 3.22 nm according to the Bragg equation.²⁴

For the HDPE/clay (100/2 w/w) system, the (001) peak still appeared at the same position as that of clay, indicating most of the clay is still in the original stacking condition.³⁸ It became blunt and its intensity was obviously lowered. After clay was com-

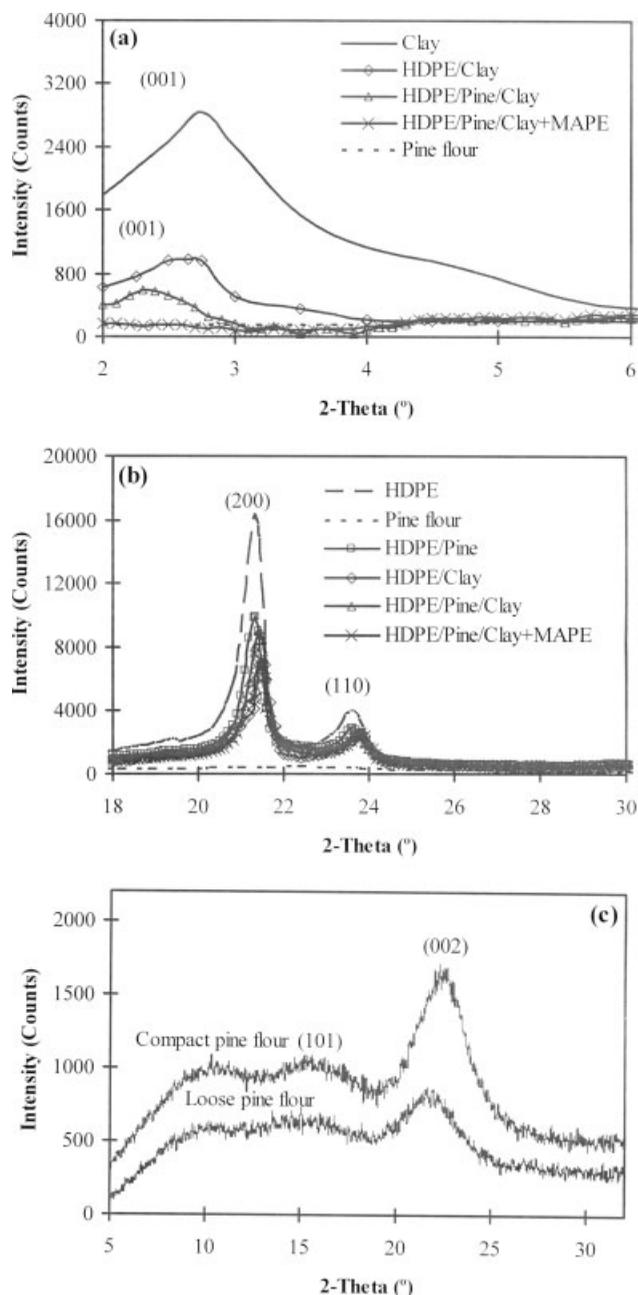


Figure 2 XRD patterns of the clay, HDPE, wood, and HDPE composites at (a) 2° – 6° and (b) 18° – 30° , and of (c) compact and loose pine and bagasse at $2^\circ/\text{min}$.

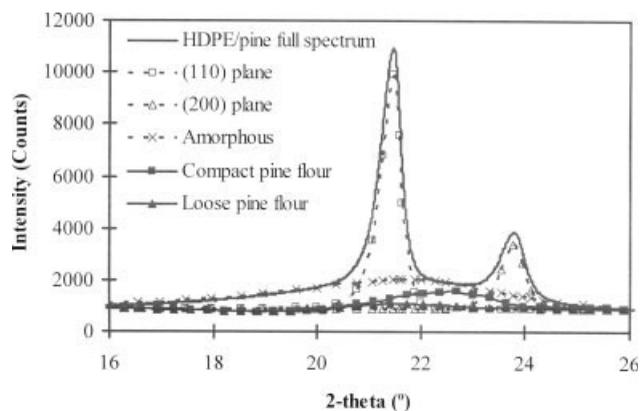


Figure 3 XRD peak separation treatment of HDPE/pine/clay composites.

pounded with HDPE and pine flour, the position of the (001) peak shifted to a lower angle of 2.3° , corresponding to a d -spacing of 3.85 nm. This means that the interlayer distance of clay increased. However, the clay was not exfoliated since the (001) peak still obviously existed. The increase of the interlayer distance might result from the stronger shear during processing when 30% pine flour was introduced. With the addition of MAPE, the (001) peak disappeared, indicating that the clay was exfoliated.

MAPE molecules could enter and penetrate the galleries between clay layers when the clay was premixed with MAPE because of the driving force, which originated from the strong hydrogen bonding between the maleic anhydride group (or COOH group generated from the hydrolysis of the maleic anhydride group) and the oxygen groups of the silicates.³⁹ The interlayer spacing of the clay increased, and the interaction of the layers should be weakened. HDPE molecules could then enter the galleries of the clay during the second compounding step, and the clay was exfoliated. Thus, proper compatibilizers were necessary to prepare HDPE/wood composites containing exfoliated clay.

Effect of clay and wood on HDPE crystallization

The XRD patterns in the 2θ range of 20° – 25° for HDPE and its composites are presented in Figure 2b. The peaks corresponding to the (110) and (200) lattice planes for HDPE are clearly apparent. Adding a small amount of clay did not affect their position but decreased their intensity suggesting the same crystal structure but lower crystallinity in the clay hybrid.

There is a potential complication in analyzing the XRD pattern for the composites containing 30% pine. Wood cell walls consist mostly of cellulose, hemicellulose, and lignin. Although hemicellulose and lignin are amorphous, cellulose has both amorphous and crystalline regions that have diffraction peaks over-

lapping those of HDPE. Figure 2c shows the XRD pattern for the pine flour as received. The peaks at about 16° and 22° corresponded to the (101) and (002) lattice plane of cellulose, respectively.⁴⁰ The diffraction pattern for compacted pine flour was also determined. Obviously, the peak intensities were higher after compaction (Fig. 2c) since the density of the wood is increased resulting in more crystalline cellulose per thickness.

The relative peak positions of the HDPE and pine flour are shown in Figure 3. Since only 30% of the pine flour is added to the HDPE, the peak intensity for the wood component would be expected to be only about 30% of that shown for the compacted pine. Compared with HDPE, the relative intensity for wood was minimal. A multiplex separation program (MDI Jade 5.0) was used to separate the crystallization peaks from the amorphous background, which included cellulose (002) lattice peak, as shown in Figure 3. The crystal thickness perpendicular to the reflection plane, L_{hkl} , was calculated using Scherrer's equation.⁴¹ The results are summarized in Table I. The influence on HDPE crystallization behavior was further explored by DSC, and the DSC cooling curves of HDPE, MAPE and their composites are shown in Figure 4. The crystallinity level (χ_c) of the HDPE matrix was evaluated from the following relationship:

$$\chi_c = \frac{\Delta H_{\text{exp}}}{\Delta H} \times \frac{1}{W_f} \times 100\%$$

where ΔH_{exp} is the experimental heat of fusion or crystallization determined from DSC, ΔH is the assumed heat of fusion or crystallization of fully crystalline HDPE (293 J/g), and W_f is the weight fraction of RHDPE in the composites. The corresponding results are listed in Table II.

As shown in Tables I and II, for HDPE, the values of L_{hkl} were 16.0 nm for the (110) lattice plane and

TABLE I
Crystalline Peaks and Thickness of HDPE and Its Composites

System ^a	Peak position θ ($^\circ$)		Crystalline thickness (nm)	
	(110)	(200)	L_{110}	L_{200}
HDPE	10.67	11.80	16.0	13.9
HDPE/pine	10.66	11.81	17.4	16.1
HDPE/clay	10.68	11.84	14.1	12.4
HDPE/pine/clay	10.71	11.88	17.5	15.4
HDPE/pine/clay/MAPE	10.68	11.86	16.4	15.3

^a The weight ratio of HDPE and pine in the composites containing pine was 70 : 30; MAPE concentration was 2% based on the total weight of HDPE and pine; clay content was 2% based on the HDPE weight.

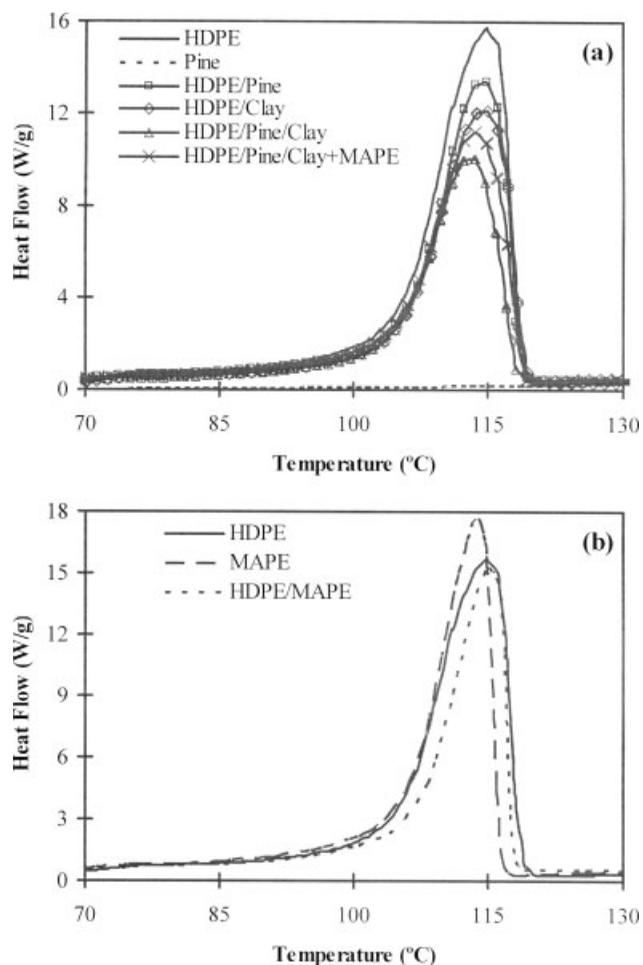


Figure 4 DSC curves of (a) wood, HDPE, and HDPE blends with pine and/or clay and (b) HDPE, MAPE, and HDPE/MAPE blend for a cooling rate of 10°C/min in N₂.

13.9 nm for the (200) lattice plane, and the crystallization peak temperature (T_c) and χ_c were 115.0°C and 59.0%, respectively. The addition of 30% pine flour increased the values of L_{hkl} to 17.4 nm for the (110) plane and 16.1 nm for the (200) plane, and the T_c and χ_c hardly changed. The addition of 30% pine flour would certainly increase the matrix viscosity at the

crystallization temperature, and would reduce the diffusion rate of the PE chain. As a result, the crystallization rate was obviously lowered (Fig. 3). The increased period might result from the poor nucleating ability of wood fiber.⁴² When 2% clay was added to pure HDPE, both values of L_{hkl} were lowered, as well as the χ_c . The same phenomenon was noticed by Lee et al.³⁶ The lowered L_{hkl} might result from the polymer nucleation by the clay, and the reduced χ_c might be ascribed to the crystal imperfection by clay.

With the addition of 2% clay to the HDPE/pine system, the crystalline thickness did not change. The T_c , crystallization rate, and χ_c decreased. It was reported that clay, especially the exfoliated clay, increased the crystallization temperature and acted as a nucleating agent.^{37,38} Since the chain mobility of HDPE was greatly reduced by the addition of 30% pine flour, the obvious chain mobility reductions might be expected when adding 2% clay. It was believed that the influence of reduced chain mobility on T_c overwhelmed that of the nucleation, resulting in the lowered T_c and crystallization rate.

With the addition of MAPE to the HDPE/pine/clay system, the crystallization rate increased (Fig. 3), but χ_c was lowered. The crystalline thickness and T_c barely changed. The T_c of pure MAPE was about 114°C, and its χ_c was 54.4%, as shown in Table II. When 2% MAPE was introduced into HDPE, the T_c and crystallization rate of HDPE barely changed, but the χ_c was lowered to 52.6%, suggesting that the MAPE reduced the perfection of HDPE crystals. When 2% MAPE was added to HDPE/pine/clay system, the increased crystallization rate suggested that exfoliated clay and pine flour with the aid of MAPE nucleated PE and lowered PE crystal perfection.⁴²

Effect of clay on mechanical properties of HDPE/pine composites

The mechanical properties of HDPE/pine composites containing different contents of clay are listed in Table III. The addition of clay increased the flex-

TABLE II
Crystallization Peak Temperatures and Levels of HDPE in Different Systems by DSC

Systems ^a	Crystallization peak temperature (°C)	Crystallization enthalpy (J/g)	Crystallinity level (%)
HDPE	115.0	172.8	59.0
HDPE/pine	114.4	170.4	58.2
HDPE/clay	114.7	152.7	52.1
HDPE/pine/clay	113.1	158.3	54.0
HDPE/pine/clay/MAPE	113.6	146.4	50.0
MAPE	113.9	159.5	54.4
HDPE/MAPE	115.1	154.1	52.6

^a The weight ratio of HDPE and pine in the composites containing pine was 70 : 30; MAPE concentration was 2% based on the total weight of HDPE and pine or HDPE weight; clay content was 2% based on the HDPE weight.

TABLE III
Mechanical Properties of HDPE/Pine/Clay Composites^{a,b}

Clay content (%)	Flexural strength (MPa)	Flexural modulus (GPa)	Tensile strength (MPa)	Tensile modulus (GPa)	Tensile elongation (%)	Impact strength (kJ/m ²)	Storage modulus (GPa)	Loss modulus (GPa)
0	31.60(c)	1.52(b)	18.09(c)	1.95(b)	3.68(b)	4.66(a)	1.91(a)	0.17(a)
1	37.79(a)	1.53(b)	22.46(a)	2.18(a)	4.16(a)	4.31(b)	1.85(a)	0.17(a)
2	36.83(a,b)	1.61(b)	21.95(a)	2.23(a)	4.04(a)	4.24(b)	1.92(a)	0.17(a)
3	35.85(b)	1.69(a)	21.02(b)	2.30(a)	3.85(a,b)	4.23(b)	1.75(b)	0.16(a)

^a The weight ratio of HDPE and pine in the composites containing pine was 70 : 30; MAPE concentration was 2% based on the total weight of HDPE and pine.

^b Means with the same letter for each property were not significantly different at the 5% significance level.

ural strength and tensile strength of HDPE/pine composites. When 1% clay was added, the flexural strength and the tensile strength increased 19.6% and 24.2%, respectively, and they had maxima at between 1 and 3% clay loading level. The addition of 1% clay increased tensile modulus 11.8% and tensile elongation 13%. The flexural and tensile moduli increased slowly with the increase of clay content, but the storage and loss moduli remained at the same level at 1–3% clay loadings. Although the impact strength was lowered 7.5% by the addition of 1% clay, it did not decrease further when the clay content was increased from 1 to 3%. The increase in mechanical properties beyond 1–2% clay loading level was not found from this study. However, others who have investigated similar composites have reported increases with up to 5% clay and much higher MAPE levels.⁴³ This may suggest that higher MAPE contents are required because of the rapidly increasing interfacial area as clay is added.

As shown in Table IV, 2% MAPE barely improved the mechanical properties of the HDPE/pine composite. The coupling agent, 2% MAPE, improved the mechanical properties of the HDPE/pine composite more than the 2% clay, which was not exfoliated (Fig. 1). Adding 2% clay to the HDPE/pine/MAPE system increased the flexural strength and tensile strength by about 17 and 21%, respectively, when a two-step process was used to ensure that the clay was exfoliated. The impact strength did not change much. Thus, the exfoliated clay reinforced the composites much more than the intercalated one.²⁷ The standard deviations were lowered when MAPE was introduced into HDPE/pine or HDPE/pine/clay system, as shown in Table IV. Since both pine and clay can interact with MAPE, there is the possibility that this competition could negatively affect dispersion when both fillers are added. However, the HDPE/pine/MAPE/clay composites had the best mechanical performance and small standard deviations suggesting good filler-matrix bonding and good filler dispersion. However, further investigation of the MAPE level would be useful in optimizing composite performance.

Effect of clay on moisture stability of HDPE/pine composites

The influence of clay on the moisture stability of the HDPE/pine composite is shown in Figure 5. There seemed to exist two stages for the increase of both moisture content (MC) and thickness swelling (TS) as a function of time, although a more in-depth investigation is warranted to verify this behavior. In stage I, the MC and TS of the composites first increased quickly, and then leveled off. The water absorption for this stage likely occurred in the sur-

TABLE IV
Mechanical Properties of HDPE and Its Composites

System ^a	Flexural strength (MPa)	Flexural modulus (GPa)	Tensile strength (MPa)	Tensile modulus (GPa)	Tensile elongation (%)	Impact strength (kJ/m ²)
HDPE	21.71 (0.85)	0.64 (0.06)	16.98 (0.17)	0.37 (0.01)	11.69 (0.24)	12.70 (0.28)
HDPE/pine	26.61 (1.01)	1.52 (0.12)	15.39 (0.39)	1.82 (0.05)	3.08 (0.39)	3.16 (0.42)
HDPE/pine/clay	28.53 (1.02)	1.44 (0.13)	16.93 (0.37)	1.99 (0.04)	3.89 (0.29)	4.12 (0.43)
HDPE/pine/MAPE	31.60 (0.63)	1.52 (0.08)	18.09 (0.23)	1.95 (0.03)	3.68 (0.23)	4.66 (0.23)
HDPE/pine/MAPE/clay	36.83 (0.50)	1.61 (0.07)	21.95 (0.18)	2.23 (0.02)	4.04 (0.21)	4.24 (0.24)

^a The weight ratio of HDPE and pine in the composites containing pine was 70 : 30; MAPE concentration was 2% based on the total weight of HDPE and pine; clay content was 2% based on the HDPE weight. The values in parentheses are standard deviation.

face layer. The MC difference between the HDPE/pine and the HDPE/pine/clay systems was increased with time, and the influence of the clay content from 1 to 3% on MC was small. The TS of HDPE/pine composite was lowered with the increase in clay content up to 2%. In stage II, the MC and TS of HDPE/pine composite containing 1% clay increased with time, but those containing 2 and 3% clay increased very slowly. At this stage, moisture most likely penetrated deeper into the composites where the exfoliated clay could create longer moisture diffusion paths and slow moisture penetration.³⁰

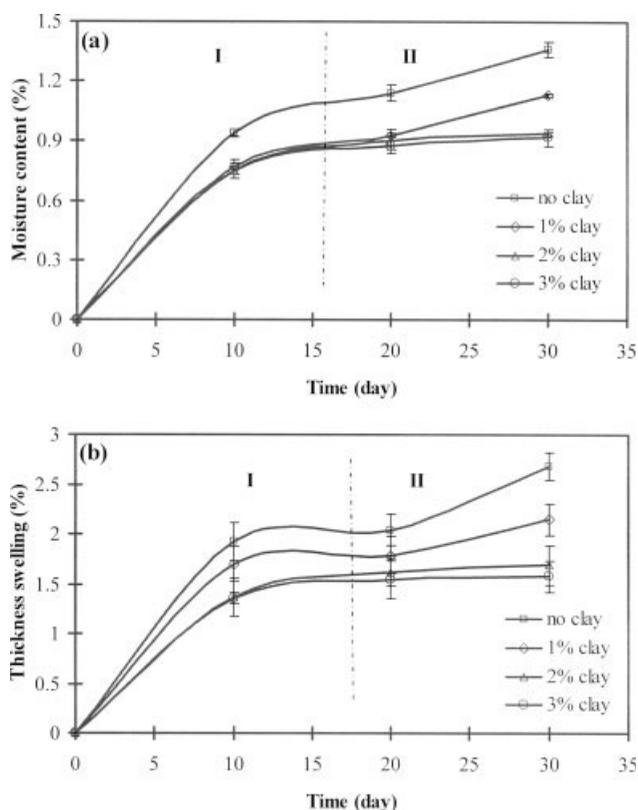


Figure 5 Effects of the clay content on (a) moisture content and (b) thickness swelling of the HDPE/pine/clay composites.

When 2% clay was added, the MC and TS of the HDPE/pine composite were lowered about 31 and 41%, respectively, after a 30-day treatment in water.

Effect of clay on thermogravimetric behavior of HDPE/pine composites

The thermogravimetric curves are plotted in Figure 6 and the results are summarized in Table V. The degradation of neat HDPE began at 444.7°C, and the maximum decomposition rate appeared at 470.4°C.

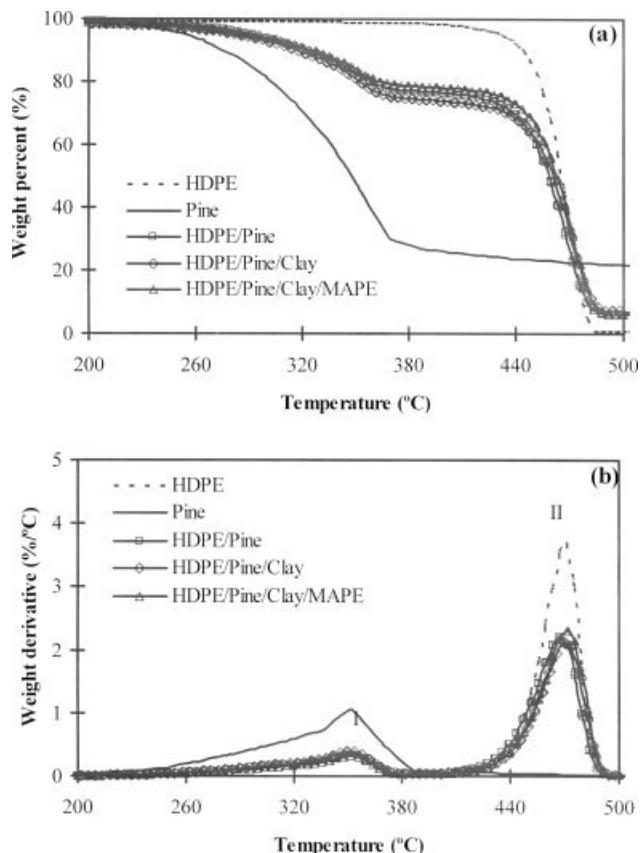


Figure 6 Temperature dependence of (a) weight loss and (b) its first derivative with respect to temperature for HDPE and its composites at 10°C/min in N₂.

TABLE V
Thermal Degradation Temperatures and Residue Weight
of HDPE and Its Composites

System ^a	T_d^b (°C)	Peak temp.(°C)		Residual (%)
		Peak I	Peak II	
HDPE	444.7	–	470.4	0
Pine	256.5	351.7	–	15.4
HDPE/pine	267.7	352.5	468.2	5.8
HDPE/pine/clay	263.7	351.6	470.9	6.4
HDPE/pine/clay/MAPE	263.3	352.1	471.5	6.4

^a The weight ratio of HDPE and pine in the composites containing pine was 70 : 30; MAPE concentration was 2% based on the total weight of HDPE and pine; Clay content was 2% based on the HDPE weight.

^b Initial thermal degradation temperature.

The initial degradation temperature (T_d) of the pine flour was 256.5°C and the decomposition peak temperature (T_p) appeared at 351.7°C. Because of the carbonization of pine fiber, the residual weight was 15.4%. There were two degradation peaks for the composites containing pine fiber. The first peak appeared at about 351–352°C starting at 263–268°C because of the wood degradation, and the other appeared at about 470°C resulting from the HDPE decomposition. Compared with the pure wood, the increased T_d for HDPE/pine system was due to the HDPE coating on the wood surface. As listed in Table V, the addition of 2% clay slightly lowered the T_d and the first decomposition peak temperature of HDPE/pine composite possibly because of the release of the low-molecular-weight compounds, with which the clay was treated to become organic, and the increased residual weight was due to the inorganic compounds in clay. The addition of compatibilizer, MAPE, had little influence on the decomposition behavior of HDPE/pine composite containing 2% clay.

CONCLUSIONS

In this study, the HDPE/pine composites containing exfoliated clay were melt compounded and then injection molded. A two-step procedure and the use of a coupling agent were necessary to produce HDPE/composites with exfoliated clay. The influence of clay on crystallization behavior, mechanical properties, water absorption, and thermal stability of HDPE/pine composites were investigated.

With the addition of 2% clay into HDPE/pine system, the crystal thickness hardly changed, but the T_c , crystallization rate, and crystallinity level decreased. When 2% MAPE was added, the crystal thickness decreased slightly and the crystallinity level was further lowered although the crystallization rate was increased.

When 1% clay was added, the flexural and tensile strengths increased 19.6% and 24.2%, respectively, but then decreased slightly as the clay content increased to 3%. The addition of 1% clay increased tensile modulus 11.8% and tensile elongation 13%. The flexural and tensile moduli increased slowly with the increase of clay content, but the storage and loss moduli remained at the same level at 1–3% clay loading levels. Although the impact strength was lowered 7.5% by the addition of 1% clay, it was not lowered further when the clay content increased from 1 to 3%. The state of dispersion in HDPE/pine/clay composites was improved by MAPE because it could interact with pine flour in addition to clay. Despite possible negative affects due competition between pine and clay for MAPE, the HDPE/pine/MAPE/clay composites still yielded the best mechanical performance. Adding 2% clay reduced the MC and TS of the HDPE/pine composite by about 31 and 41%, respectively, after 30-day water treatment. However, the clay did not improve the thermal stability of the HDPE/pine composite.

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