PROPERTIES OF HDPE/CLAY/WOOD NANOCOMPOSITES

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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 were investigated. The HDPE/pine composites containing exfoliated clay were made by a two-step melt compounding procedure with a maleated polyethylene (MAPE) as a compatibilizer. Adding 2% clay to a HDPE/pine composite without MAPE decreased the crystallization temperature ($T_c$) and rate, and the crystallinity level. When 2% MAPE was added, the $T_c$ and crystallization rate increased, but the crystallinity level was lowered. The flexural strength and the tensile strength of HDPE/pine composites increased 19.6% and 24.2% respectively with addition of 1% clay but then decreased slightly as the clay content was increased to 3%. The tensile modulus and tensile elongation were increased 11.8% and 13% respectively with addition of 1% clay but the storage and loss moduli barely change as the clay content was increased to 3%. The impact strength was lowered 7.5% by adding 1% clay, but did not decrease further as more clay was added. The moisture content and thickness swelling of the HDPE/pine composites was reduced by the clay, but did not improve the thermal stability.

Keywords: 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, having 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 (WPC) 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) (PVC),¹²⁻¹³ polystyrene (PS),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,\textsuperscript{17-21} as well as improving processing methods.\textsuperscript{22,23}

The 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 to conventional composites.\textsuperscript{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 introducing compatibilizers containing polar groups, such as maleated polyethylene (MAPE), carboxylated PE, etc.\textsuperscript{31-38}

Wang et al.\textsuperscript{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 and coworkers\textsuperscript{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.\textsuperscript{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.\textsuperscript{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.\textsuperscript{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.

\section*{EXPERIMENTAL}
\subsection*{Materials}
High density polyethylene (grade HD6605) with a melt index of 5 g/10min (190°C, 2.16 kg) and a density of 0.948 g/cm\textsuperscript{3} was obtained from ExxonMobil Chemical. Cloisite\textsuperscript{®} 15A, a natural montmorillonite modified with a dimethyl-dihydrogenated tallow-ammonium chloride, was obtained from Southern Clay Products, Inc.. Less than 10\% of the dry clay particles are greater than 13 micrometer in diameter. A maleated polyethylene (MAPE) compatibilizer (Polybond\textsuperscript{®} 3009) with a melt index of 5 g/10min (190°C, 2.16 kg) and 1.0wt\% maleic anhydride was obtained from Crompton-Uniroyal Chemical. Pine (\textit{Pinus sp}..) flour with a nominal 20-mesh particle size from American Wood Fibers Company was used in the experiment.

\subsection*{Preparation of HDPE/Pine/clay composites}
A 1-L thermokinetic high-shear mixer (a K-mixer from Synergistics Industries) was used to blend the composites. The raw materials were compounded in the thermokinetic mixer at 5,000 rpm and discharged when a temperature of 190°C was reached. The blending was completed in one step for all the systems except for the system 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 the other materials in a second step to achieve the targeted
formulations. Based on the HDPE weight, the loading level of clay was 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.

Before injection molding, the blends were milled to pass a screen with 1cm 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 2? range from 2º to 40º in reflection mode was scanned at 2º/min. A computer-controlled wide angle goniometer coupled to a sealed-tube source of Cu-Kα radiation (λ=1.54056Å) was used. The Cu-Kα 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 0.16º. 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°C 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 (TGA) was employed to observe the thermal character of hybrids with a TA Q50 Thermogravimetric Analyzer under nitrogen at a scan rate of 10 °C/min from room temperature to 650°C. Samples of 6-8 mg were 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 Company, Horsham, PA) was used for the Izod impact test. All the samples were notched on the center 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 minutes at -1.0×10⁴ Pa, and then impregnated with water before the vacuum was released. 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 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 2? range of 2º to 32º spectrum are shown in Figure 1. The peaks appearing at 2-3º correspond to clay, and the strong peaks appearing at about 21.3º and 23.6º are from the (110) lattice plane and (200) lattice
plane of HDPE crystals, respectively. Figure 2(a) and 2(b) show the measured intensity data over the characteristic 2θ range for clay, and RHDPE and wood, respectively. As Figure 2(a) shown, a strong peak was present at the position of 2.75º for clay, which corresponds to a d-spacing of 3.22 nm according to the Bragg equation:

$$2d \sin \theta = n \lambda$$  \hspace{1cm} (1)

where $d$ is the distance between crystallographic planes, and $\theta$ is half of the angle of diffraction, $n$ is an integer, and $\lambda$ is the wavelength of the X-ray.

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. It became blunt and its intensity was obviously lowered. After clay was compounded with HDPE and pine flour, the position of the (001) peak shifted to a lower angle of 2.3º, 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. Because of the strong interaction between clay layers and MAPE molecules, MAPE molecules could enter and penetrate the gallery between clay layers when the clay was premixed with MAPE. 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 20º to 25º for HDPE and its composites are presented in Figure 2(b). 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 that overlap those of HDPE. Figure 2(c) shows the XRD pattern for the pine flour as received. The peaks at about 16º and 22º corresponded to the (101) and (002) lattice plane of cellulose, respectively. Since the wood flour is densified during processing, the diffraction pattern for compacted pine flour was also determined. Not surprisingly, the peaks for the pine flour increased with density.

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 and its relative intensity was minimal. A multipeak 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:

$$L_{hkl} = \frac{K\lambda}{\beta_0 \cos \theta}$$  \hspace{1cm} (2)

$$\beta_0^2 = \beta_M^2 - \beta_I^2$$  \hspace{1cm} (3)
where $\beta_0$ is the width of the diffraction beam (rad); $\beta_M$ is the measured width of the diffraction beam (rad); $\beta_I$ is the instrumental broadening (rad); $K$ is the shape factor of crystalline thickness, related to $\beta_0$ and $L_{hkl}$. When $\beta_0$ is defined as the half-height width of the diffraction peak, $K=0.9$. The results are summarized in Table 1.

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 of the HDPE matrix was obtained by dividing the value of crystallization heat by 293 J/g, the assumed heat of crystallization for 100% crystalline PE and was adjusted for the weight fraction of HDPE in the composites. The corresponding results are listed in Table 2.

As shown in Table 1 and 2, for HDPE, the values of $L_{hkl}$ were 16.0 nm for the (110) lattice plane and 13.9 nm for the (200) lattice plane, and the crystallization peak temperature ($T_c$) and crystallinity level 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 $T_c$ became 114.4°C. 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 $T_c$ shifted to a lower temperature, and the crystallization rate was obviously lowered (Figure 3). The increased period might result from the poor nucleating ability of wood fiber and crystal imperfection. When 2% clay was added to pure HDPE, both values of $L_{hkl}$ were lowered, as well as the crystallinity level. The same phenomenon was noticed by Lee et al. The lowered $L_{hkl}$ and crystallinity level were a result of the reduced crystallization rate (Figure 3).

With the addition of 2% clay to the HDPE/pine system, the crystalline thickness perpendicular to the (110) plane remained the same level, while that for (200) plane decreased. The $T_c$, crystallization rate, and crystallinity level also decreased. It was reported that clay, especially the exfoliated clay, increased the crystallization temperature and acted as a nucleating agent. 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 crystalline thickness perpendicular to the (200) lattice plane was at the same level, but that for (110) lattice plane decreased. The $T_c$ increased to 113.6°C, and the crystallinity level was lowered from 54.0% to 50.0%. The $T_c$ of pure MAPE was about 114°C, and its crystallinity level was 54.4%, as shown in Table 2. When 2% MAPE was introduced into HDPE, the $T_c$ and crystallization rate of HDPE barely changed, but the crystallinity level was lowered to 52.6%, suggesting that the MAPE did not nucleate crystal growth in HDPE and that MAPE reduced the perfection of HDPE crystals. When 2% MAPE was added to RHDPE/pine/clay system, the lowered $L_{hkl}$ and increased $T_c$ and crystallization rate suggested that exfoliated clay and pine flour with the aid of MAPE nucleated HDPE.

**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 3 and are shown in Figure 5. The addition of clay increased the flexural 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 1-3% clay. 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 as shown.
in Figure 4, but the storage and loss moduli stayed at almost the same level at 1-3% clay. 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% was not found for our composites. However, others who have investigated similar composites have reported increases with up to 5% clay and much higher MAPE levels. This may suggest that complete exfoliation is not achieved in our composites with 3% clay content or that higher MAPE contents are required due to the rapidly increasing interfacial area as clay is added.

**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 6. There seemed to exist two stages for the increase of both moisture content (MC) and thickness swelling (TS) versus 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 surface layer. The MC difference between the HDPE/pine system 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. When 2% clay was added, the MC and TS of the HDPE/pine composite were lowered about 31% and 41%, respectively, after 30-day treatment in water.

**Effect of clay on thermogravimetric behavior of HDPE/pine composites**

The thermogravimetric curves are plotted in Figure 7 and the results are summarized in Table 4. The degradation of neat HDPE began at 444.7°C, and the maximum decomposition rate appeared at 470.4°C. 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 residue 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 owing to the wood degradation, and the other appeared at about 470°C resulting from the HDPE decomposition. Compared with the neat wood, the increased $T_d$ for HDPE/pine system was due to the HDPE coating the wood. As listed in Table 4, 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 residue 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 compounding 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 perpendicular to (200) plane decreased, and the $T_c$, crystallization rate, and crystallinity level decreased. When 2% MAPE was added, the crystal thickness perpendicular to
(110) plane decreased. The $T_c$ increased slightly to 113.6°C, and the crystallinity level was lowered from 54.0% to 50.0% 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 was 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 stayed almost the same level at 1-3% clay. The limited increases in tensile and flexural properties may be due to the low MAPE content (2%) and suggests further formulation optimization. Although the impact strength was lowered 7.5% by the addition of 1% clay, it was not lowered further when the clay content was increased from 1% to 3%. Adding 2% clay reduced the moisture content and thickness swelling of the HDPE/pine composite about 31% and 41% respectively after 30-days in water. However, the clay did not improve the thermal stability of the HDPE/pine composite.

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Table 1. Crystalline Peaks and Thickness of HDPE and Its Composites.

<table>
<thead>
<tr>
<th>System</th>
<th>Peak position (º)</th>
<th>Crystalline thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(110)</td>
<td>(200)</td>
</tr>
<tr>
<td>HDPE</td>
<td>10.67</td>
<td>11.80</td>
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<tr>
<td>HDPE/Pine</td>
<td>10.66</td>
<td>11.81</td>
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<td>HDPE/Clay</td>
<td>10.68</td>
<td>11.84</td>
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<td>HDPE/Pine/Clay</td>
<td>10.71</td>
<td>11.88</td>
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<tr>
<td>HDPE/Pine/Clay/MAPE</td>
<td>10.68</td>
<td>11.86</td>
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Table II. Crystallization Peak Temperatures and Levels of HDPE in Different Systems by DSC

<table>
<thead>
<tr>
<th>Systems</th>
<th>Crystallization peak temperature (°C)</th>
<th>Crystallization enthalpy (J/g)</th>
<th>Crystallinity level (%)</th>
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</thead>
<tbody>
<tr>
<td>HDPE</td>
<td>115.0</td>
<td>172.8</td>
<td>59.0</td>
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<tr>
<td>HDPE/Pine</td>
<td>114.4</td>
<td>170.4</td>
<td>58.2</td>
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<td>HDPE/Clay</td>
<td>114.7</td>
<td>152.7</td>
<td>52.1</td>
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<td>HDPE/Pine/Clay</td>
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<td>158.3</td>
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<td>HDPE/Pine/Clay/MAPE</td>
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<td>MAPE</td>
<td>113.9</td>
<td>159.5</td>
<td>54.4</td>
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<tr>
<td>HDPE/MAPE</td>
<td>115.1</td>
<td>154.1</td>
<td>52.6</td>
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</table>

Table III: Mechanical Properties of HDPE/Pine/Clay Composites

<table>
<thead>
<tr>
<th>Clay Content (%)</th>
<th>Flexural Strength (MPa)</th>
<th>Flexural Modulus (GPa)</th>
<th>Tensile Strength (MPa)</th>
<th>Tensile Modulus (GPa)</th>
<th>Tensile Elongation (%)</th>
<th>Impact Strength (MPa)</th>
<th>Storage Modulus (GPa)</th>
<th>Loss Modulus (GPa)</th>
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</thead>
<tbody>
<tr>
<td>0</td>
<td>31.60(c)</td>
<td>1.52(b)</td>
<td>18.09(c)</td>
<td>1.95(b)</td>
<td>3.68(b)</td>
<td>4.66(a)</td>
<td>1.91(a)</td>
<td>0.17(a)</td>
</tr>
<tr>
<td>1</td>
<td>37.79(a)</td>
<td>1.53(b)</td>
<td>22.46(a)</td>
<td>2.18(a)</td>
<td>4.16(a)</td>
<td>4.31(b)</td>
<td>1.85(a)</td>
<td>0.17(a)</td>
</tr>
<tr>
<td>2</td>
<td>36.83(a,b)</td>
<td>1.61(b)</td>
<td>21.95(a)</td>
<td>2.23(a)</td>
<td>4.04(a)</td>
<td>4.24(b)</td>
<td>1.92(a)</td>
<td>0.17(a)</td>
</tr>
<tr>
<td>3</td>
<td>35.85(b)</td>
<td>1.69(a)</td>
<td>21.02(b)</td>
<td>2.30(a)</td>
<td>3.85(a,b)</td>
<td>4.23(b)</td>
<td>1.75(b)</td>
<td>0.16(a)</td>
</tr>
</tbody>
</table>

*The values in parentheses are standard deviation. Means with the same letter for each property were not significantly different at the 5% significance level.

Table IV: Thermal Degradation Temperatures and Residue Weight of HDPE and Its Composites

<table>
<thead>
<tr>
<th>System</th>
<th>$T_d$ a (°C)</th>
<th>Peak Temp. (°C)</th>
<th>Residue (%)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Peak I</td>
<td>Peak II</td>
</tr>
<tr>
<td>HDPE</td>
<td>444.7</td>
<td>—</td>
<td>470.4</td>
</tr>
<tr>
<td>Pine</td>
<td>256.5</td>
<td>351.7</td>
<td>—</td>
</tr>
<tr>
<td>HDPE/Pine</td>
<td>267.7</td>
<td>352.5</td>
<td>468.2</td>
</tr>
<tr>
<td>HDPE/Pine/Clay</td>
<td>263.7</td>
<td>351.6</td>
<td>470.9</td>
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<tr>
<td>HDPE/Pine/Clay/MAPE</td>
<td>263.3</td>
<td>352.1</td>
<td>471.5</td>
</tr>
</tbody>
</table>

*a. Initial thermal degradation temperature.
Figure 1  XRD patterns of the clay, HDPE, wood, and HDPE composites at 2 °/min for 2° angles of 2° to 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.
Figure 2  XRD patterns of the clay, HDPE, wood, and HDPE composites at (a) 2° to 6° and (b) 18° to 30°, and of (c) compact and loose pine and bagasse at 2°/min. 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 3  XRD peak separation treatment of HDPE/pine/clay composites. 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 N\textsubscript{2}. 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 5  Effects of the clay content on the mechanical properties of the HDPE/pine composites. 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.
Figure 6  Effects of the clay content on (a) moisture content and (b) thickness swelling of the HDPE/pine/clay composites. 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.
Figure 7  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. 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.