INFLUENCE OF LIGNIN CONTENT ON PHOTODEGRADATION IN WOOD/HDPE COMPOSITES UNDER UV WEATHERING

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The aim of this work was to examine the influence the lignin component of wood on the photodegradation of high-density polyethylene (HDPE) in wood/HDPE (WPE) composites. The neat HDPE and wood/HDPE composites were prepared using a twin screw extruder followed by an injection moulder. The lignin content was varied from 0 to 29 %wt. of wood by the addition of delignified wood pulp into wood flour. The results suggested that the photodegradation of HDPE in WPE composites was accelerated by the presence of lignin; the chromophoric groups in the lignin enhanced UV adsorption onto the WPE composite surface. The carbonyl and vinyl indices, color, percentage crystallinity, and the melting temperature increased when the lignin contents were increased. The color fading in WPE composites resulted from photobleaching of lignin. In addition, the presence of lignin led to the development ofl cracks in WPE composites, especially at high lignin contents. For the effect of UV weathering time, the carbonyl and vinyl indices, discoloration, and percentage crystallinity increased as a function of UV weathering times, whereas the melting temperature of HDPE in both neat HDPE and WPE composites and water absorption of specimens decreased; the wood index in WPE composites increased during the initial UV weathering times and then decreased at 720 h weathering time.

Keywords: Wood flour; High density polyethylene; Lignin; Composite; Photodegradation; UV weathering

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INTRODUCTION

Wood/polymer composite (WPC) is one of the currently favored materials for use in decorations, buildings, and construction applications. This is because of the many advantages of WPC, such as low production and maintenance costs, environmental friendliness, and good dimensional stability. However, there are a number of external factors that affect the mechanical and physical properties of the WPC articles. For example, UV light, moisture, and heat are significant factors that lead to changes in mechanical and physical properties (Muasher and Sain 2006; Stark 2006; Sombatsompop et al. 2008; Mulinari et al. 2010; Zabihzadeh 2010; Wang et al. 2010; Chaochanchaikul et al. 2011b). Therefore, the applications of WPC require knowledge about the durability of these WPC products after weathering.

There are many publications related to the photodegradation in WPC that have revealed that the fading of color and the loss of mechanical properties occur from UV light and moisture (Stark and Matuana 2004a,b; Muasher and Sain 2006; Stark 2006; Ndiaye et al. 2008; Wang et al. 2010; Chaochanchaikul et al. 2011a; Pattamasattayasonti et al. 2011).

High density polyethylene (HDPE) is one of the commodity plastics that has been incorporated with natural fibers to produce WPC. Photo-degradation in HDPE is mainly caused by the chromophoric groups, such as, catalyst residues, hydroperoxide and carbonyl groups, and double bonds (Valadez-Gonzalez et al. 1999; Stark and Matuana 2004a). The initial hydroperoxide and carbonyl groups and double bonds are formed as the result of the thermo-mechanical degradation that arises during processing (Valadez-Gonzalez et al. 1999). The carbonyl groups are claimed to be the main chromophoric groups responsible for the photochemical induced degradation reactions of UV-exposed polymers (Khan and Ahmed 2003; Stark and Matuana 2004a).

UV radiation at the wavelength of 313 nm has sufficient energy to break the C-C bonds in the polymer, but the alkane will not absorb in this wavelength region. However, when a carbonyl group absorbs light in this region it can cause the breaking of a C-C bond adjacent to the carbonyl bond (Khan and Ahmed 2003). The degradation reactions of HDPE proceed from the carbonyl group precursor according to Norrish type I and II (Valadez-Gonzalez et al. 1999; Khan and Ahmed 2003; Stark and Matuana 2004a,b; Muasher and Sain 2006). The photo-degradation of HDPE is a result of competing reactions between chain scission and crosslinking that lead to changes in molecular weight and crystallinity (Valadez-Gonzalez et al. 1999; Stark and Matuana 2004a; Muasher and Sain 2006; Wang et al. 2010). Under UV weathering, the addition of degraded, recycled HDPE in virgin HDPE showed more rapid photodegradation than virgin HDPE and the blend containing un-degraded, recycled HDPE (Craig and White 2006). The previously photodegraded HDPE acts as a pro-degradant. The formed functional groups on the surface of HDPE after UV irradiation were C=O and C-O (1730 and 1180 cm^{-1}, respectively) (Jelle and Nilsen 2011; Li et al. 2011). Their contents and crystallinity increased with increasing irradiation time, whereas the melting temperature of HDPE decreased (Li et al. 2011).

Lignin is the key structure responsible for photodegradation of wood, as lignin has the ability to absorb in the UV/visible region due to its chromophoric groups (Colom et al. 2003). The mechanism of photodegradation of lignin in wood involves two competing redox reactions upon UV weathering (Muasher and Sain 2006). The first is oxidation of lignin, which leads to the formation of paraquinone chromophoric structures within the first 250 h of UV weathering, and the second involves reduction of the paraquinone structures to hydroquinones, which leads to photobleaching after 250 h of UV weathering. The structural changes in the lignin component after UV weathering have been examined using FTIR spectroscopy and it was found that all characteristic bands of lignin (1595, 1510, and 1465 cm^{-1}) decreased with increasing UV ageing times (Colom et al. 2003). Moisture was found to accelerate the photodegradation reaction in the wood (Turkulin et al. 2004).

Studies have also focused on the various aspects affecting the color, structural, and mechanical property changes of wood/HDPE (WPE) composites, such as wood content, processing methods, weathering conditions, and time and type and content of UV absorbers and pigments (Stark and Matuana 2003, 2004a,b; Muasher and Sain 2006; Stark 2006; Stark and Matuana 2007; Ndiaye et al. 2008; Wang et al. 2009; Du et al.2010; Wang et al. 2010). The presence of wood affects the surface of WPE composites oxidized to a greater extent than that of the neat HDPE (Stark and Matuana 2004a,b). The presence of wood in WPE composites does not change the pathway of photooxidation of the HDPE, but the wood absorbed in the UV-VIS domain and could contribute to the degradation initiation through the creation of radicals (Ndiaye et al. 2008). The changes in chemical structure, color, and crystallinity of WPE composites could not be reliably used to predict changes in mechanical properties with a simple linear relationship (Stark and Matuana 2004b; Wang et al. 2010). This was because the chemical structural and crystallinity changes occurred at the surface of WPE composites by UV exposure, whereas the majority of the changes in mechanical properties after weathering were involved with interfacial degradation caused by moisture. The content or water is the important variable in the photodegradation in WPE composites by accelerating the oxidation reactions and swelling the wood cell wall to facilitate light penetration into the wood (Stark 2006). In addition, the water also washes away the degraded layer and removes wood extractives. The wood loss from the surface of extruded composites occurs more than that of injection molded composites (Stark and Matuana 2007). For the effect of surface roughness on photodegradation of WPE composite, it was found that the smooth surface of composites was more durable in mechanical properties than the sawn surface due to the presence of matrix acting as a protector (Wang et al. 2009). The addition of pigment or UV absorber could protect a HDPE matrix of WPE composites from UV degradation (Stark and Matuana 2003; Du et al. 2010; Zhang et al. 2010).

Well-documented literature indicates that the presence of wood has led to accelerated photodegradation of HDPE in WPE composites, and some of these research works (Stark and Matuana 2004a,b; Ndiaye et al. 2008) explain that the acceleration of photodegradation in HDPE is due to chromophore groups or carbonyl groups in the lignin component. In addition, the color fading of wood can be caused by photodegradation of lignin (Muasher and Sain 2006; Chaochanchaikul et al. 2011a; Pattamasattayasonti et al. 2011). This suggests that lignin is a significant component of photodegradation in WPE composites. However, most existing studies only offer qualitative explanations on the effect of lignin on the photodegradation in WPE composites. Very rarely have these studies actually been able to control the lignin content in the WPE composites and study the effect on photodegradation behaviour. Therefore, the aim of this work was to examine the effect of lignin quantity on the photodegradation of WPE composites using various techniques, such as, UV-VIS spectrophotometry, Fourier-transform infrared (FTIR) spectroscopy, Differential scanning calorimetry (DSC), and Scanning electron microscopy (SEM) techniques. To overcome a difficulty in delignifying lignin from wood flour, the lignin content was varied by adding as-received delignified wood pulp into the wood flour in the HDPE.

EXPERIMENTAL

Raw Materials

HDPE

HDPE was supplied by Dow Chemical Company (Michigan, USA) in the form of pellets under the trade name of Dowlex IP-10262 Polyethylene. The melt flow index (MFI) of the as-received HDPE was 9.0.

Wood flour particles

Wood flour particles (*Xylia kerri Craib* or *Ironwood*) from wood-working processes were supplied by V.P. Wood Company Limited (Bangkok, Thailand). The average size of wood particles used in this work was in the range of 100 to 250 μm. The lignin content in *Xylia kerri Craib wood*, as characterized by the extractive method (Hon 1996) with 96% acetic acid and sodium chlorite in a water bath between 70 to 80 °C for 3 h, was 29% by weight (%wt.).

Delignified wood pulps

Delignified wood pulps produced from *Eucalyptus* (*Eucalyptus spp.*) were supplied by Advance Agro Public Company Limited (Prachinburi, Thailand), and they were used as-received. The lignin content of the delignified wood pulps was taken to be zero in this work, as they had undergone the delignification and bleaching processes.

Blending WPE Composites

The lignin content was varied through 0, 5, 10, 20, and 29 %wt. of wood by mixing wood flour and delignified wood pulp. The ratios of wood flour and delignified wood pulp represented the lignin content as listed in Table 1. The wood content (wood flour and delignified wood pulp) added to HDPE was fixed at 20 %wt. Before blending of wood and HDPE, the wood flour and delignified wood pulp were dried in an oven at 80 °C for 24 h until the weight of the wood was constant. HDPE pellets were passed through a granulator to reduce the particle size of HDPE to be close to that of wood flour and delignified wood pulp. The granulated HDPE was dry-mixed with the wood flour and delignified wood pulp in a high-speed mixer at a mixing speed of 1000 rpm for 2 min before being melt-blended in a twin-screw extruder (LTE 26-40, Labtech Engineering Co., Ltd., Thailand) with co-rotating screws. The barrel temperatures in the extruder were set at 140, 140, 150, 150, 150, 160, 160, 170, 170, and 170 °C from hopper to die zones. The screw rotating speed was 100 rpm. A two strand die (each strand having a diameter of 3 mm) was connected at the end of the barrel, producing two extrudates at the die exit. Then, the extrudates were solidified by passing them through an air cooling system via the use of a pull-off unit and a pelletizer to produce WPE composite granules.

Specimen Production

HDPE and WPE composite specimens for the weathering test were produced in an injection moulder (Boy 50A, Boy Machines, Inc, USA). The barrel temperatures in the injection moulder were set at 170, 170, 175, and 195 °C from the hopper to the nozzle zones. The screw rotating speed used to produce the melt was 60 rpm, and the injection speed and pressure were 26 cm^3/s and 75 kg/cm^2, respectively. The dimensions of the square mould used were 12.5 x 126.0 x 3.0 mm^3.

Table 1. Ratios of Wood Flour and Delignified Wood Pulp Representing the Various Lignin Contents

Lignin content (%)	Wood flour : delignified wood pulp weight ratio
0	0.0:20.0
5	3.5:16.5
10	6.9:13.1
20	13.8:6.2
29	20.0:0.0

Weathering Test

The HDPE and WPE specimens were weathered in a QUV weatherometer (QUV/SE, Q-panel Lab Products, Inc, USA) operated according to ASTM G154 (2006). The HDPE and WPE specimens were weathered in a cyclic UV/condensation exposure consisting of 8 h of UV light exposure at 60 °C with the 313 nm fluorescent UVB lamps followed by 4 h of condensation at 50 °C. The UV irradiation intensity was 0.71 W/m^2 at 313 nm. The changes in color, chemical structure, and physical properties of the weathered HDPE and WPE specimens were then evaluated as a function of UV weathering time ranging from 0 to 720 h. The UV weathering time used in this work was the sum of the UV radiation and the condensation time.

Characterizations

Color analysis

The color of HDPE and WPE specimens before and after UV weathering were measured using a Spectrophotometer (Konica Minolta CM-700d Spectrophotometer, Japan) according to the CIE LAB color system. The $L^*a^*b^*$ coordinates of unweathered and weathered HDPE and WPE composite specimens were calculated based on a D65 light source. L^* represents the lightness, whereas a^* and b^* are coordinates of the hue. The higher the L^* value the lighter the sample. The a^* coordinate represents red-green coordinate while the b^* coordinate represents yellow-blue coordinate. The total color changes or discolorations of the UV-weathered specimens were calculated from differences in lightness and chromatic coordinates (ΔE) of unweathered and weathered HDPE and WPE composite specimens by Equation 1 (Chaochanchaikul et al. 2011a). The reported color data in each condition were averaged from measurements on three independent specimens and the measurement on each specimen was carried out in three different positions,

$$\Delta E = \sqrt{(L_2^* - L_1^*)^2 + (a_2^* - a_1^*)^2 + (b_2^* - b_1^*)^2} \tag{1}$$

where subscript 1 denotes the values for unweathered specimens and subscript 2 denotes the values for weathered specimens.

Structural change analysis

The structural changes in un-weathered and weathered specimens were estimated using attenuated total reflectance FTIR (ATR-FTIR) Spectrometer (Nicolet 8700 FT-IR spectrometer, USA) with a diamond crystal. The extent of degradation of HDPE in neat HDPE and WPE composites was assessed by considering the carbonyl and vinyl indices. The reported data were averaged from five independent determinations. In this work, carbonyl and vinyl indices shown in Equations 2 and 3 were calculated by subtracting the value of % absorbance of the peak of interest from the baseline ($\%A_{1720}$ and $\%A_{908}$, respectively) and dividing it by the reference value which was also subtracted from the baseline ($\%A_{2920}$). The wavenumbers of 1720, 908, and 2920 cm^{-1} were assigned for carbonyl and vinyl groups and C-H stretching, respectively (Stark and Matuana 2004b).

$$\textit{Carbonyl index} = \frac{\%A_{1720}}{\%A_{2920}} \tag{2}$$

$$\textit{Vinyl index} = \frac{\%A_{908}}{\%A_{2920}} \tag{3}$$

In addition to carbonyl and vinyl indices, the intensity of the peak at 1051 cm^{-1} was observed as a function of weathering time. This peak represents C-O stretching mainly in cellulose and hemicellulose and C-O deformation in lignin (Stark and Matuana 2007; Du et al. 2010). Therefore, the wood index was calculated using Equation 4 (Du et al. 2010).

$$\textit{Wood index} = \frac{\%A_{1051}}{\%A_{2920}} \tag{4}$$

Crystallinity content and melting temperature

The crystallinity contents and the melting temperatures of HDPE in neat HDPE and WPE composites were estimated by differential scanning calorimetry (DSC). Before DSC analysis, the weathered surfaces (≈ 50 μm thick) were removed from the specimens using a cryogenic microtome (Bright Startlet 2212 Cryostat Microtome, Bright Instrument Co., Ltd., United Kingdom). The crystalliniy contents and the melting temperatures of HDPE in neat HDPE and WPE composites before and after weathering were analyzed with a DSC analyzer (TA Instruments Q1000 DSC analyzer, USA) according to ASTM

D3418. The weathered surfaces were heated from 20 ^{o}C to 200 ^{o}C at a heating rate of 10 ^{o}C/min. The percentage crystallinity (X) was determined from Equation 5 (Li et al. 2011),

$$X = \frac{H_m}{H_m^{\,o} x\ w} x100 \qquad (5)$$

where H_m is the melting enthalpy of the sample, H_m^{o} is the melting enthalpy at 100% crystallinity of HDPE, which is 285.9 J/g (Li et al. 2011), and w is weight fraction of the HDPE in WPE composites.

Water absorption

Three specimens of dimensions 15 x 20 x 2.7 mm^3 for each formulation were used for measuring water absorption. The specimens before and after weathering were dried in an oven at 50 ^{o}C for 24 h until the specimen weight was constant. After that the specimens were placed in deionized water at room temperature. The immersion times were varied as 0, 2, 4, 6, 24, 48, and 72 h. For each measurement, the specimens were removed from the water and the surface water was wiped off using blotting paper. The percentage water absorption of the specimens was determined by weighing the specimens to a precision of 0.1 mg. The water absorption at any time ($WA(t)$) was calculated using Equation 6,

$$WA(t) = \frac{W(t) - W_0}{W_0} x100 \qquad (6)$$

where W_0 is the oven dried weight and $W(t)$ is the weight of specimen at a given immersion time t.

Surface analysis

The specimen surfaces of unweathered and weathered WPE composites were studied after being sputtered with gold and analyzed with an environmental SEM (FEI Quanta 200F, USA) at 10 kV accelerating voltage.

RESULTS AND DISCUSSION

Color Analysis

Figure 1 shows the lightness ($L*$) of HDPE and WPE composites as a function of UV weathering times. It was found that the initial $L*$ values of HDPE and WPE composites of 0 %wt. lignin (without wood flour) were obviously higher than that of WPE composites containing wood flour due to the differences in the initial colors of HDPE, delignified wood pulp, and wood flour. The $L*$ values of WPE composites of high lignin contents tended to increase with increasing UV weathering times, whereas those of neat HDPE and WPE composites of low lignin contents (0 to 10 %wt. of lignin) were relatively unchanged. The color fading of WPE composites of high lignin contents was attributed to photodegradation or photobleaching of lignin in the wood flour, which resulted from the transformation of the paraquinone to hydroquinone structures (Muasher and Sain 2006; Bengtsson et al. 2007; Chaochanchaikul et al. 2011a). Figure 2 shows that the increases in total color change (*ΔE*) as a function of UV weathering were caused by the photodegradation of HDPE, delignified wood pulp, and wood flour. The values of *ΔE* in the case of HDPE and WPE composites of low lignin contents (0 to 5 %wt.) changed only slightly compared to those of WPE composites of high lignin contents. This implied that the lignin played a significant role in the photodegradation of WPE composites.

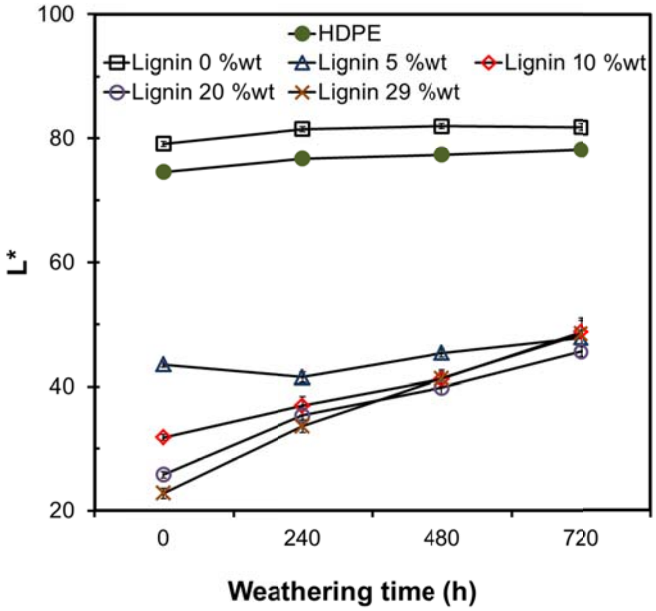

Fig. 1. Lightness of HDPE and WPE composites of various lignin contents as a function of UV weathering times

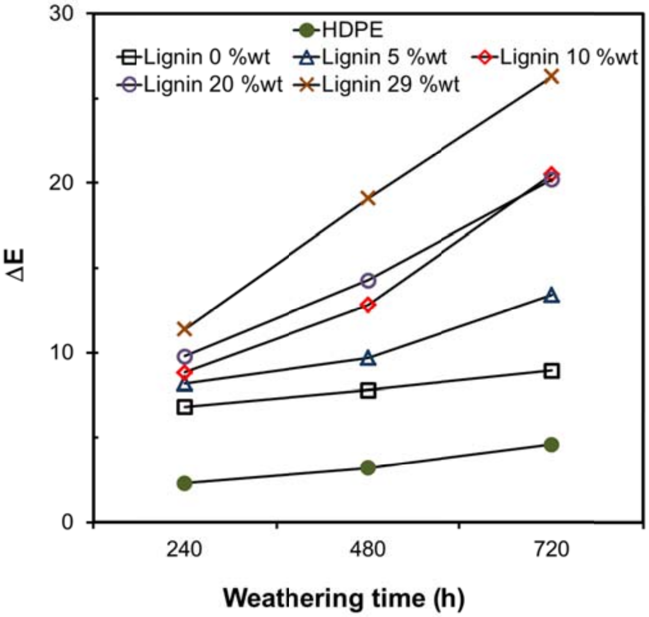

Fig. 2. Discoloration level of HDPE and WPE composites of various lignin contents as a function of UV weathering times

It appears that the chromophoric groups in lignin enhanced UV absorption onto the surface. This could be confirmed by Fig. 3, which suggested that the color fading of WPE composites at 720 h weathering time was the highest in the case of 29 %wt. of lignin, although its initial color was the darkest. The changes in *ΔE* values of WPE composites were found to correspond to the changes in *L** values.

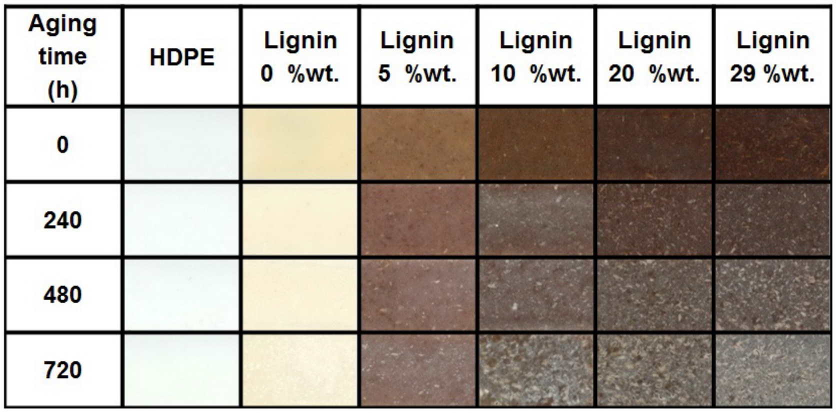

Fig. 3. Digital photos of HDPE and WPE composite specimens at different UV weathering times

Structural Change Analysis

The changes in the chemical structure of the specimen surfaces were directly used for analyzing the degradation of the WPE composites. Carbonyl groups are considered to be the main light-absorbing species responsible for the photochemical induced degradation reactions in polymers (Stark and Matuana 2004a). Figure 4 shows the carbonyl index of neat HDPE and WPE composites at various UV weathering times.

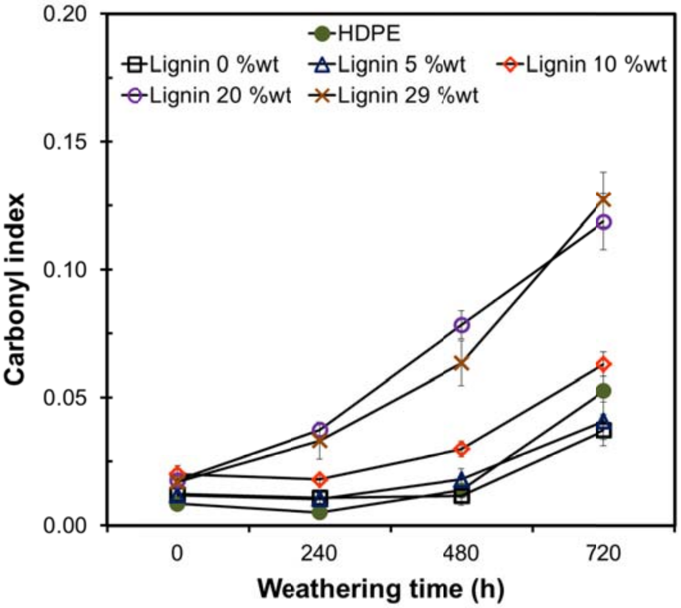

Fig. 4. Effect of lignin content on carbonyl index in HDPE and WPE composites

Before weathering, the carbonyl contents of all the formulations were similar, although the lignin itself has carbonyl groups. This might be attributed to the HDPE matrix at the surface encapsulating wood flour and delignified wood pulp. If this is the case, the use of ATR-FTIR spectrometer as the mode of investigation at the specimen surface only might not be able to detect the differences in carbonyl contents in specimens containing different lignin contents. The carbonyl indices of neat HDPE and WPE composites increased as the UV weathering times were increased. The effect of UV weathering time on the carbonyl index could be easily observed in the case of WPE composites of high lignin contents (20 to 29 %wt.), whereas they could be seen in the cases of neat HDPE and WPE composites of low lignin contents at high weathering times only. The presence of carbonyl groups in lignin accelerated photodegradation in HDPE, as it is a UV absorbing species. The results in Fig. 4 revealed that the critical lignin content to affect the photodegradation in HDPE was greater than 10 %wt.

The vinyl group is another functional group occurring during photodegradation of HDPE, as shown in Fig. 5. It was found that the vinyl index increased with increasing UV weathering time and lignin content. The effect of lignin content on the vinyl content during weathering could not be seen as obviously as those on the carbonyl content. This was because the measured carbonyl content by ATR-FTIR was obtained from the carbonyl group in the weathered HDPE and the protruding wood particles after weathering, whereas the vinyl content was obtained from weathered HDPE only. This explanation could be well supported by the result of wood index, as shown in Fig. 6. Wood index was estimated from the peak at 1051 cm^{-1} as a result of C-O stretching in cellulose and hemicellulose and C-O deformation in lignin (Stark and Matuana 2007; Du et al. 2010). The wood index in WPE composites tended to increase at the initial weathering times and then decrease at the 720 h weathering time. The changes in wood index could be explained by Fig. 7, which shows the surfaces of WPE composites before and after the 720 h weathering time. Figure 7b reveals that a wood particle had protruded at the surface of the weathered WPE composite, and voids had also occurred at the surface of the weathered WPE composite. The increases in wood index at initial UV weathering times were caused by the protrusion of wood components (wood flour and/or delignified wood pulp) at the surface of WPE composites. After weathering, the attacked HDPE under UV light became more brittle, and the wood components were swelled by moisture during condensation. These factors might have created the pressure at the wood-HDPE interface, which caused the microcracks around the wood particles within the HDPE matrix. The cracked HDPE at the surface could have been washed away during weathering, and that led to protrusion of wood components. The significant decrease in wood index at UV weathering time of 720 h resulted from the looseness of the protruded wood components, which probably resulted from highly degraded HDPE. Both components (protruded wood and HDPE) were washed away by condensation during weathering.

Figure 8 shows SEM micrographs of neat HDPE and WPE composites before weathering and after weathering at 720 h. Cracks were revealed on the surfaces for both neat HDPE and WPE composites after weathering. The amount of cracks increased with increasing lignin content as shown by a comparison between Figs. 8b, 8d, 8f, and 8h. The surfaces of the weathered neat HDPE and WPE composite of lignin content of 0 %wt. had microcracks only, whereas that of the weathered WPE composite of lignin content of 5 and 29 %wt. had both cracks and protruding wood particles. The cracks on the surface of the WPE composite of lignin content of 29 %wt. were most pronounced, which was expected based on the explanation given for Fig. 7.

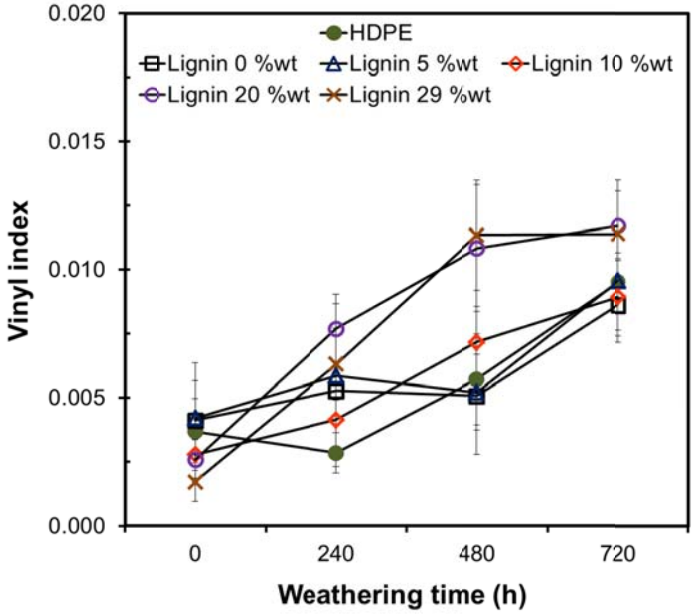

Fig. 5. Effect of lignin content on vinyl index in HDPE and WPE composites

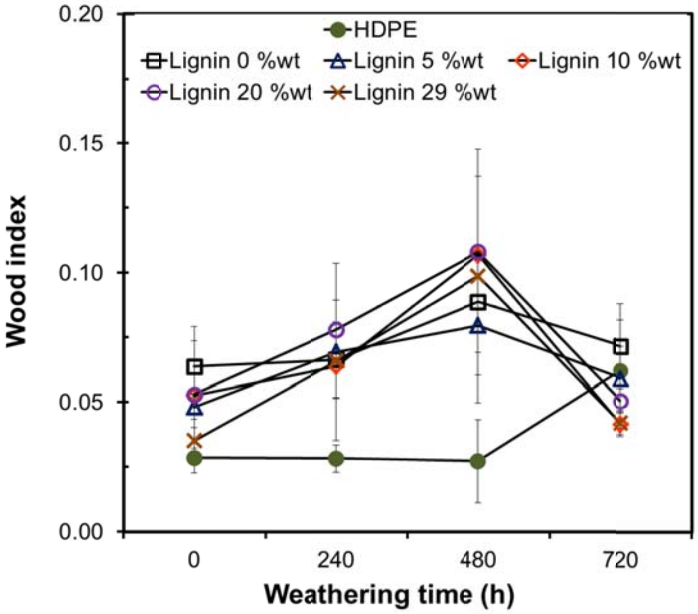

Fig. 6. Wood index of surface of WPE composites at different UV weathering times

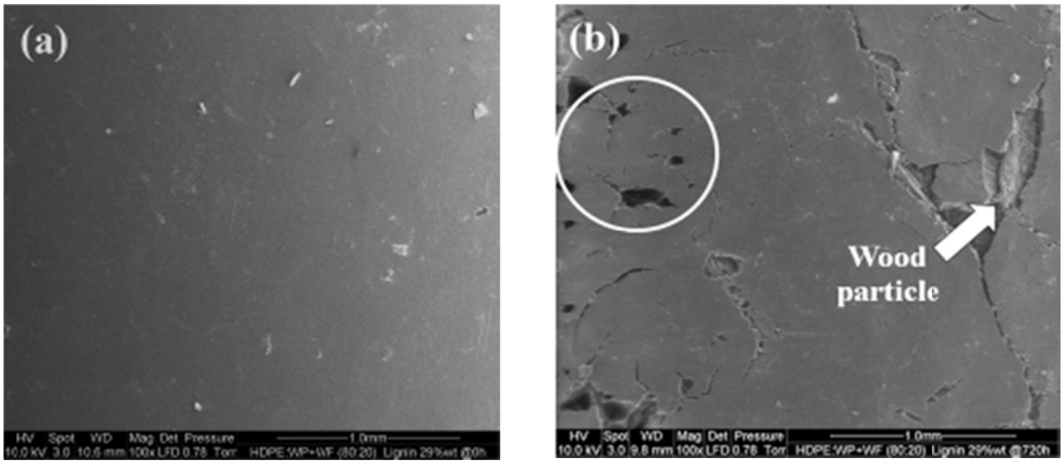

Fig. 7. SEM micrographs of surfaces of WPE composites of lignin content of 29 %wt. before and after UV weathering at 100x magnification: (a) Before UV weathering; (b) After 720 h UV weathering time

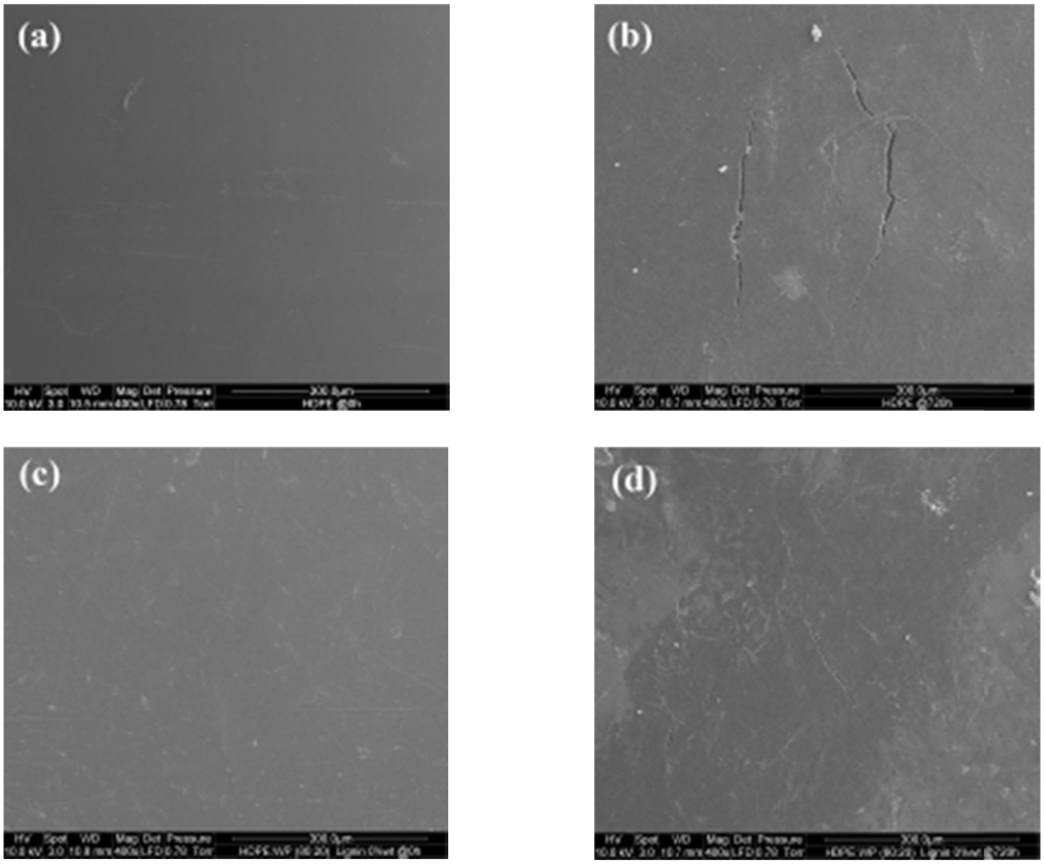

Fig. 8 (a-d). SEM micrographs of surfaces of neat HDPE and WPE composites before and after UV weathering at 400x magnification: (a), (c), (e), and (g) before UV weathering of neat HDPE and WPE composites of lignin content of 0, 5, and 29 %wt., respectively; (b), (d), (f), and (h) after 720h UV weathering time of neat HDPE and WPE composites of lignin content of 0, 5, and 29 %wt., respectively

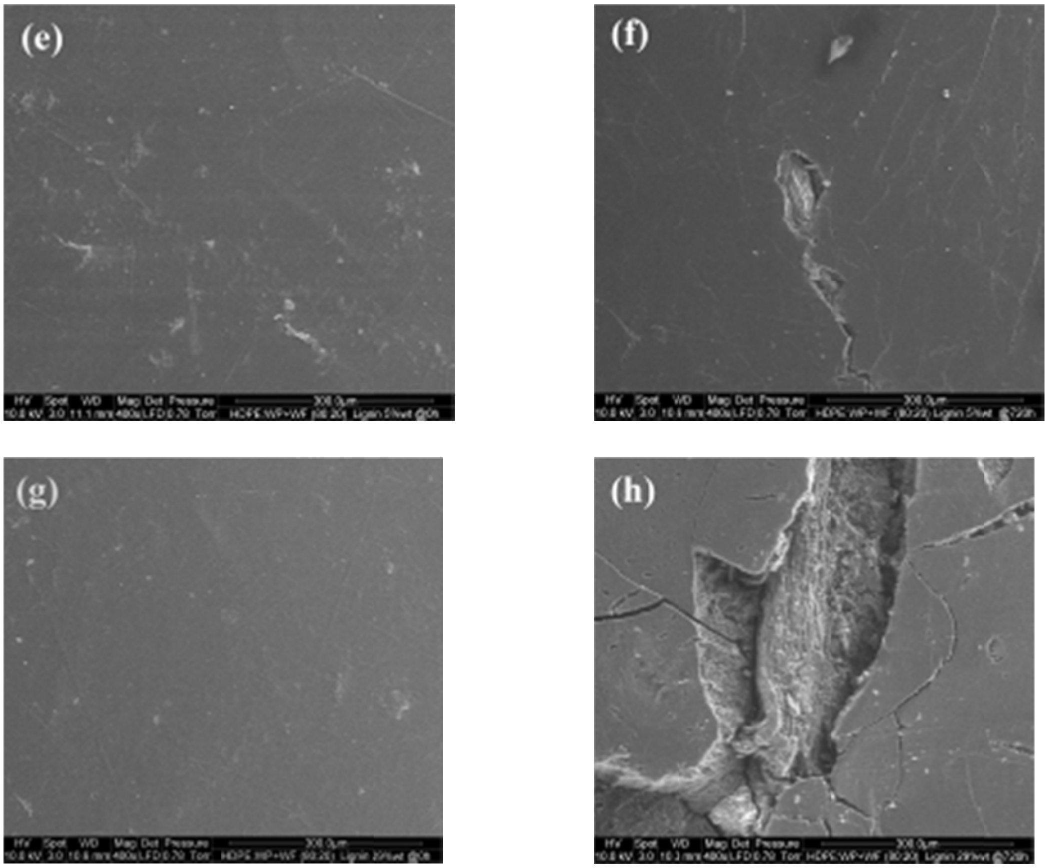

Fig. 8 (e-h). SEM micrographs of surfaces of neat HDPE and WPE composites before and after UV weathering at 400x magnification: (a), (c), (e), and (g) before UV weathering of neat HDPE and WPE composites of lignin content of 0, 5, and 29 %wt., respectively; (b), (d), (f), and (h) after 720h UV weathering of neat HDPE and WPE composites of lignin content of 0, 5, and 29 %wt.

Percentage Crystallinity and Melting Temperature

Figure 9 shows the changes in percentage crystallinity of HDPE measured by DSC for neat HDPE and WPE composites as a function of UV weathering time. The percentage crystallinities of HDPE tended to increase with increasing UV weathering time. Based on previous work (Stark and Matuana 2004a; Muasher and Sain 2006; Li et al. 2011), an increase in percentage crystallinity could be due to the chain scission and also annealing effect during weathering to facilitate the recrystallization of HDPE chains. In this work, the increase in crystalline content of HDPE for both neat HDPE and WPE composites under UV weathering might be mainly caused by the annealing effect during the initial stages, and partially by the chain scission upon prolonged UV ageing, considering the results of carbonyl and vinyl contents in Figs. 4 and 5. At low lignin content (0 to 5 %wt.), it was found that the percentage crystallinity of HDPE increased at initial UV weathering times (0 h to 240 h) and then slightly changed for higher weathering times (480 to 720 h), except for the specimen at 0%wt of lignin. The percentage crystallinity of HDPE in WPE composites of high lignin contents (10 to 29 %wt.) increased continually with increasing UV weathering time; the higher the lignin content, the higher the crystalline content except for 240 h UV weathering time.

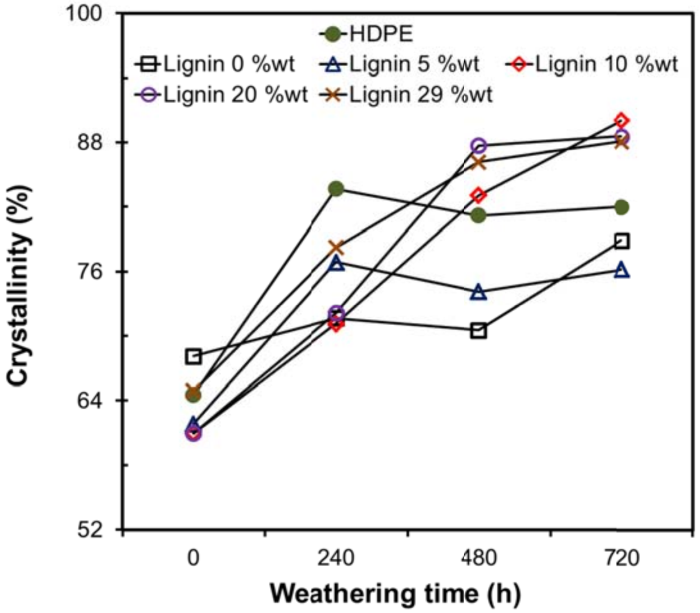

Fig. 9. Percentage crystallinity of HDPE in HDPE and WPE composites as a function of UV weathering times by DSC analysis

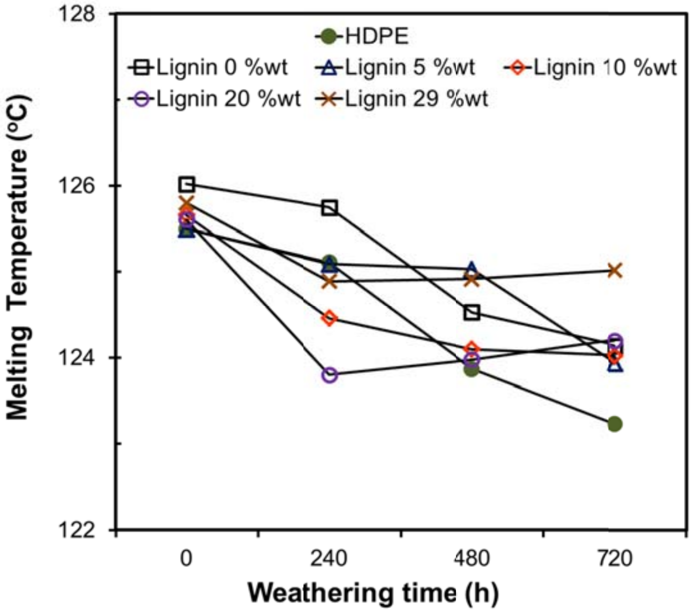

Fig. 10. The onset melting temperatures of HDPE and WPE composites as a function of UV weathering times

It should be noted that at 0 to 240 h UV, the effect of molecular annealing appeared to be more pronounced than that of chain scission, and this caused the higher percentage crystanility for neat HDPE compared with that for HDPE in WPE composites. The results in Figure 9 indicated that the specimens with higher lignin contents showed increasing levels of crystallinity, especially at high weathering times. The reason for that was; the fact that the chromophore groups in the lignin could enhance UV absorption onto the composite surface (Stark and Matuana 2004a; Ndiaye et al. 2008) and then cause photodegradation of HDPE via chain scission which promoted the ability of HDPE to crystallize.

Figure 10 shows the melting temperatures of HDPE in neat HDPE and WPE composites as a function of UV weathering time. The melting temperatures for neat HDPE and WPE composites after UV weathering were lower than those for neat HDPE and WPE composites before UV weathering. This was attributed to the UV light during weathering, which induced the chain scission of the molecules, and the chain folds at crystal surfaces led to the reduction of interchain forces. The decrease in melting temperature for neat HDPE and WPE composites of low lignin content (0-5 %wt.) started to decrease at 480 h UV weathering time, whereas the melting temperature in the case of WPE composites of high lignin content (10-29 %wt.) began to decrease at 240 h UV weathering time. This difference indicated that the higher the lignin contents the faster the HDPE degradation during weathering.

Water Absorption

Figure 11 shows the water absorption for neat HDPE and WPE composites of lignin contents of 0 and 29 %wt. before and after UV weathering. The increase in water absorption in both neat HDPE and WPE composites could be seen when the immersion time increased, especially the initial immersion time (before 6 h). The water absorption of neat HDPE and WPE composites increased in the order: WPE composite of lignin content of 0 %wt. > WPE composite of lignin content of 29 %wt. > neat HDPE. The differences in water absorption were simply explained by the differences in the chemical structures of these three materials. The WPE composite of lignin content of 0 %wt. was a HDPE/delignified wood pulp composite, whereas the WPE composite of lignin content of 29 %wt. was a HDPE/wood flour composite. The delignified wood pulp is composed of cellulose and hemicellulose as the main components, while the wood flour is composed of lignin, cellulose, and hemicellulose. Cellulose and hemicellulose have more hydrophilic groups such as hydroxyl groups, while lignin has phenol rings, which are hydrophobic (Shafiei et al. 2010). HDPE is classified as a hydrophobic material considering the chemical structure as a hydrocarbon.

Under UV weathering, it was found that water absorption of WPE composites with lignin contents of both 0 and 29 %wt. after 720 h weathering time was lower than that of WPE composites before weathering, whereas the water absorption of neat HDPE before and after weathering was only slightly different. The decrease in water absorption of the WPE composites after weathering might be attributed to the increase in crystallinity in HDPE after weathering. The crystalline structure makes it difficult for the water to diffuse into the WPE specimen, although there were some voids in the WPE composites. This indicated that the effect of crystallinity of HDPE in WPE composites on water absorption was more dominant than the voids that had occurred. The differences in water absorption of unweathered and weathered WPE composites of lignin content of 29 %wt. was higher than that of WPE composites of lignin content of 0 %wt. This result also corresponded well with the result of percentage crystallinity as shown in Fig. 9.

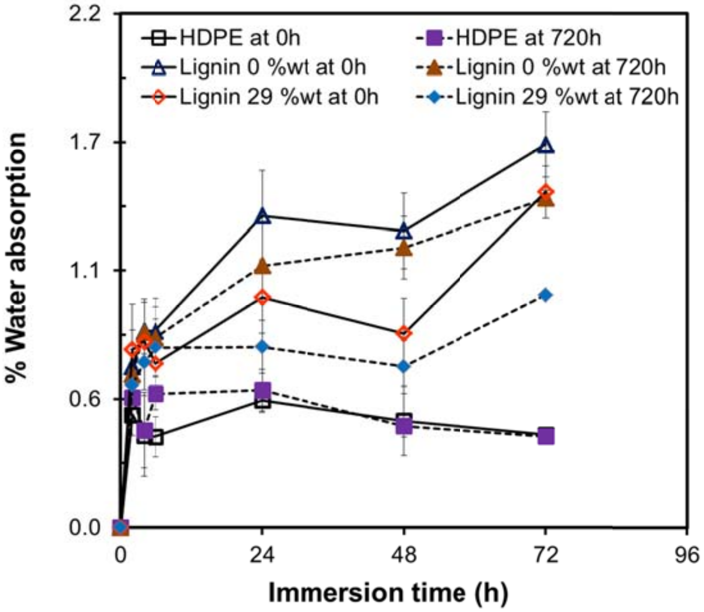

Fig. 11. Water absorption of HDPE and WPE composites before and after 720 h UV weathering time

CONCLUSIONS

The influence of lignin content on photodegradation of HDPE in WPE composites was estimated using spectrophotometric, FTIR, DSC, and SEM techniques, as well as water absorption. The experimental results suggested that the lignin in WPE composites accelerated the photodegradation of HDPE. The color fading in WPE composites resulted from photobleaching of lignin. The protrusion of wood particles onto the WPE composite surface after UV weathering led to an increase in wood index during the initial UV weathering time. Cracks at the WPE composite surfaces were observed in the WPE composites, especially at high lignin contents. The carbonyl and vinyl indices, discoloration, and percentage crystallinity tended to increase with increasing UV weathering times from 0 to 720 h, whereas the melting temperature of HDPE in both neat HDPE and WPE composites and water absorption of specimens decreased; wood index in WPE composites increased at the initial UV weathering times and then decreased at 720 h weathering time.

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