

Effects of Pigments on the UV Degradation of Wood-Flour/HDPE Composites

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ABSTRACT: The effects of different color pigments on the durability of wood-flour/high-density polyethylene composites (WF/HDPE) were evaluated by UV-accelerated weathering tests. WF/HDPE composites were dyed using three different color inorganic pigments, which were added at 2% based on the weight of the composite. Samples were weathered in Q-panel UV aging equipment for 1500 h. All samples showed significant fading and color changes in exposed areas. Changes in surface chemistry were studied using spectroscopic techniques. X-ray photoelectron spectroscopy (XPS) was used to verify the occurrence of surface oxidation. Changes in carbonyl groups (C=O), PE crystallinity, cellulose C—O, and lignin aromatic C=C were detected by Fourier transform infrared (FTIR) spectroscopy. The results indicate that surface ox-

idation occurred immediately within exposure 250 h for all samples; the surface of the control WF/HDPE composites was oxidized to a greater extent than that of the dyed WF/HDPE. This suggests that the addition of pigments to the WF/HDPE composites results in less weather-related damage. The surface configuration observed by scanning electron microscopy revealed that WF/HDPE composites degraded significantly on accelerated UV aging, with dense cracking apparent on the exposed surface. Carbon black had a more positive effect on color stability than the other pigments. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 1068–1076, 2010

Key words: wood-flour/HDPE; composite; pigment; UV weathering; color; photodegradation

INTRODUCTION

Wood-plastic composites (WPCs) are increasingly accepted and used for the manufacture of interior parts such as flooring, handrails, and decorative components in China as low-maintenance and high-durability building products. The market for exterior products made from WPCs such as decking and garden furniture is also expanding rapidly in China because they are environmentally friendly. However, WPCs suffer from color change and a loss of mechanical properties during long-term outdoor applications. Thus, the durability of these products against exposure, particularly to UV light is of wide concern. Some researchers have found that WPCs exposed to accelerated weathering undergo a color change^{1–4} and a loss of mechanical properties.^{1–7} Surface chemistry changes of wood-flour (WF)-filled poly(vinyl chloride)/polyethylene has been investigated.^{6–11} Crystallinity changes in wood-fiber-filled polyethylene after weathering have also been stud-

ied.^{8,9,12} The results demonstrate that UV exposure can cause photodegradation of both the polymer matrix and the wood in the surface of WPCs, which may lead to discoloration,^{2–10} making the products esthetically unappealing. Furthermore, prolonged UV exposure may ultimately lead to loss of mechanical integrity.^{2–5,7}

Photostabilizers are compounds that can protect polymers from UV degradation. The main types of photostabilizers are UV absorbers (UVAs), quenchers, and free-radical scavengers. In addition, pigments are also often used as photoblockers to inhibit the photodegradation of plastics.⁹ Muasher and Sain investigated the efficacy of photostabilizers in preventing color changes in wood-filled plastic composites.¹³ High molecular weight diester hindered-amine light stabilizers (HALS) were found to be most effective in controlling long-term fading and yellowing. The addition of a benzotriazole UV absorber to diester HALS shows synergistic effect on decreasing color fading. Stark and Matuana investigated the effectiveness of photostabilizers including two different HALS: one UVA and one colorant on the UV stability of high-density polyethylene (HDPE)-filled WF.⁵ These results indicated that both colorant and ultraviolet absorber were more effective photostabilizers for WF/HDPE composites than HALS.

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Some researchers have incorporated pigments to improve wood-plastic composite weathering; few compared different pigments and focused on the evaluation of color and property change in WPCs.³ In this study, we not only compare the effect of three different color pigments on lightness of WF/HDPE composite but also try to investigate the chemical structural changes in detail during weathering. Changes in carbonyl groups (C=O), PE crystallinity, cellulose C—O, and lignin aromatic C=C groups were detected by Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). The results reported here will promote our understanding of the efficiency of pigments in protecting WPCs against exposure to UV radiation.

EXPERIMENTAL

Materials

The HDPE (density 0.954, melting flow index 0.9 g/min) material used in this study was supplied by Petrifaction Company (DaQing, China) and WF of 50–80 mesh was procured from the local timber market. Three inorganic pigments colcothar (a dark red pigment, which is basically composed of ferric oxide), carbon black, and titanium dioxide were purchased from domestic company. Maleic anhydride grafted polyethylene (MAPE) with grafting ratio 0.9% was used as coupling agent, which was supplied by Guangzhou Bochen Company.

Processing

The WF was dried for 24 h at 105°C to decrease the moisture content to ~ 0.9% (dry weight basis) before the compounding process. Composite formulations were prepared containing 2% (w/w) pigment (colcothar, carbon black, or titanium dioxide), 50% (w/w) WF, 2% (w/w) MAPE, with HDPE comprising the remainder. A control with no pigment was also prepared. WF, HDPE, MAPE, and pigment additives were dry blended in a high-intensity 10-L kinetic mixer at 3200 rpm with a tip speed of 23 m/s, respectively. The mixture was discharged at a preset temperature of 85°C and then compounded by a one-step extrusion process on a twin-screw/single-screw extruder system. Processing temperature for extrusion was set at 180°C for melting zone, 160–170°C for pumping zone and 170°C for die zone, respectively. The rotary speed of twin-screw was 150 rpm. The cross sectional area of the extruded lumber was 4.0 × 40.0 mm².

Weathering

WF/HDPE samples with dimension of 80 × 13.5 × 4 mm³, which were cut from the extruded lumber,

were placed in a Q-panel UV aging system (American) that was operated according to ASTM G154–04 and tested for up to 1500 h. The weathering cycle consisted of 8 h of dry UV exposure at 60°C, followed by 4 h of condensation exposure at 50°C without radiation. Samples were removed for analysis after 250, 500, 1000, and 1500 h of exposure and were compared with unexposed samples. The UVA 340 lamps were calibrated every 500 h.

Scanning electron microscopy

The surface of samples was sputter-coated with gold and analyzed under a scanning electron microscope (SEM; FEI QUANTA 200) at a working distance of ~ 25 mm, voltage of 15 kV, and a probe current of 6 × 10⁻¹⁰ A.

Color measurements

The surface color of the samples was measured using an NF333 photometer (Nippon Denshoku Co.) according to the CIE $L^*a^*b^*$ color system. Lightness (L^*) and chromaticity coordinates (a^* and b^*) were measured for six replicate samples. L^* represents the lightness coordinate and varies from 100 (white) to 0 (dark). a^* represents the red ($+a^*$) to green ($-a^*$) coordinate, whereas b^* represents the yellow ($+b^*$) to blue ($-b^*$) coordinate. An increase in L^* means that the sample has lightened or faded (i.e., positive ΔL^* for lightening and negative ΔL^* for darkening). Similarly, positive Δa^* represents a color shift toward red and negative Δa^* is a shift toward green. Positive Δb^* represents a color shift towards yellow and negative Δb^* is a shift toward blue. The total color change ΔE was calculated according to ASTM D2244¹⁴:

$$\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

It should be noted that ΔE^* represents the magnitude of the color difference, but does not indicate the direction of this difference.

FTIR spectroscopy

FTIR spectra (KBr disk method) were recorded on a MAGNA-IR560 (Nicolet) spectrometer to provide detailed information about functional groups at the composite surface before and after weathering. Scanning was carried out at a resolution of 4 cm⁻¹ from 4000 to 400 cm⁻¹. The peak intensity was determined by subtracting the height of the baseline from the total peak height. The same baseline was chosen for each peak before and after weathering. At least five replicate specimens were analyzed for each formulation.

TABLE I
Deconvoluted Peak Assignment, Binding Energy, and Bond Type for High-Resolution C_{1s} and O_{1s} XPS Data

Carbon group	Binding energy (eV)	Bond
C1	284.84	C—C or C—H
C2	286.13	C—O
C3	287.18	O—C—O or C=O
C4	288.38	O—C=O
O1	531.71	C=O
O2	533.28	O—C—O

X-ray photoelectron spectroscopy

X-Ray photoelectron spectra were generated using a K-Alpha spectrograph (Thermo Scientific). To determine the type of O—C bonds present, chemical bond analysis of carbon was accomplished by deconvoluting the curve into four peaks. The deconvoluted peak assignments and the corresponding binding energy and bond type are shown in Table I.

RESULTS AND DISCUSSION

SEM morphology

The microsurface of unexposed and exposed WF/HDPE composites is shown in Figure 1. Both colored and uncolored samples presented smooth and integrated surfaces before weathering [Fig. 1(a–d)]. However, uncolored WF/HDPE composites had apparent surface cracks and WF particles emerged from the surface after 1500 h of accelerated UV weathering [Fig. 1(a')]. Composites containing pigment showed fewer cracks on the surface than composites without pigment after accelerated UV weathering 1500 h [Fig. 1(a'–d')], in which carbon black presented the least cracking. This indicates that pigments can mask some UV radiation and prevent WF/HDPE against UV radiation damage in certain period and carbon black can probably absorb or shield more UV-light comparing with the other tincorial pigments. Although pigment addition to WF/HDPE as a photostabilizer could not ultimately prevent cracking on the sample surface after UV weathering, using a proper pigment could delay cracking.

Color analysis

Figure 2 shows the changes in brightness of colored and uncolored WF/HDPE composites during accelerated UV weathering. L^* increased for all composite samples, with the greatest increase observed after 500 h of exposure. Different formulations exhibited sharply different changes in L^* with increasing UV exposure. Samples containing pigment clearly showed less lightening than composites without pigment. Although the addition of colcothar or titanium

dioxide to WF/HDPE composites significantly resulted in less changes in L^* compared with unweathered control samples, these changes were much higher than that obtained from samples with carbon black. The addition of carbon black had the greatest protective effect among all the pigments, showing the least fading. It is possibly because the black pigment may shield more UV-light or screen from more composite lightening than the other tincorial pigments. Thus, proper pigments were efficient in preventing composite lightening.

Stark and Matuana reported that WPC lightening can be attributed to the chain scission of HDPE and its migration to the surface as well as to photo-bleaching of lignin.^{4,13} It is presumed that pigments can inhibit lightening by physically blocking UV radiation, resulting in less UV radiation available to bleach the samples.¹⁵

FTIR spectroscopy

FTIR spectroscopy was used to study chemical changes on the surface of WF/HDPE before and after weathering. Usually the broad peak around 3400 cm^{-1} band is associated with mixed hydroxyl groups originating mainly from cellulose and hemicellulose. The peak around 1056 cm^{-1} is characteristic peak associated with C—O stretching mainly in cellulose and hemicellulose of WFs. The peak around 1630 cm^{-1} is characteristic absorption of conjugated carbonyl group C=O of lignin in WF. The peaks around 1608 cm^{-1} and 1506 cm^{-1} represent the stretching of aromatic ring framework in lignin of WF.¹⁵ The peaks at 2917 cm^{-1} , 2850 cm^{-1} , 1472 cm^{-1} , 730 cm^{-1} , and 720 cm^{-1} are the characteristic peaks of methylene, attributed to the symmetric stretching, asymmetric stretching, in-plane deformation, rocking (crystalline), and rocking (amorphous) of C—H bond in HDPE. The important FTIR peaks and the corresponding groups and vibration type are listed in Table II. The FTIR spectra of WF, HDPE, HDPE with 2% MAPE, and unweathered control samples of WF/HDPE composites are shown in Figure 3. Because the maleated coupling agents had no significant influence on the degradation of WPC,¹⁶ its effect was not discussed here.

The intensity of the peaks at 1715 cm^{-1} and 1056 cm^{-1} that represent carbonyl (C=O) stretching and C—O stretching mainly in cellulose and hemicellulose of WFs, respectively, was measured.^{11,17,21,18} The carbonyl index and wood index were calculated using the following equations, respectively^{8,21}:

$$\text{Carbonyl index} = \frac{I_{1715}}{I_{2912}} (100)$$

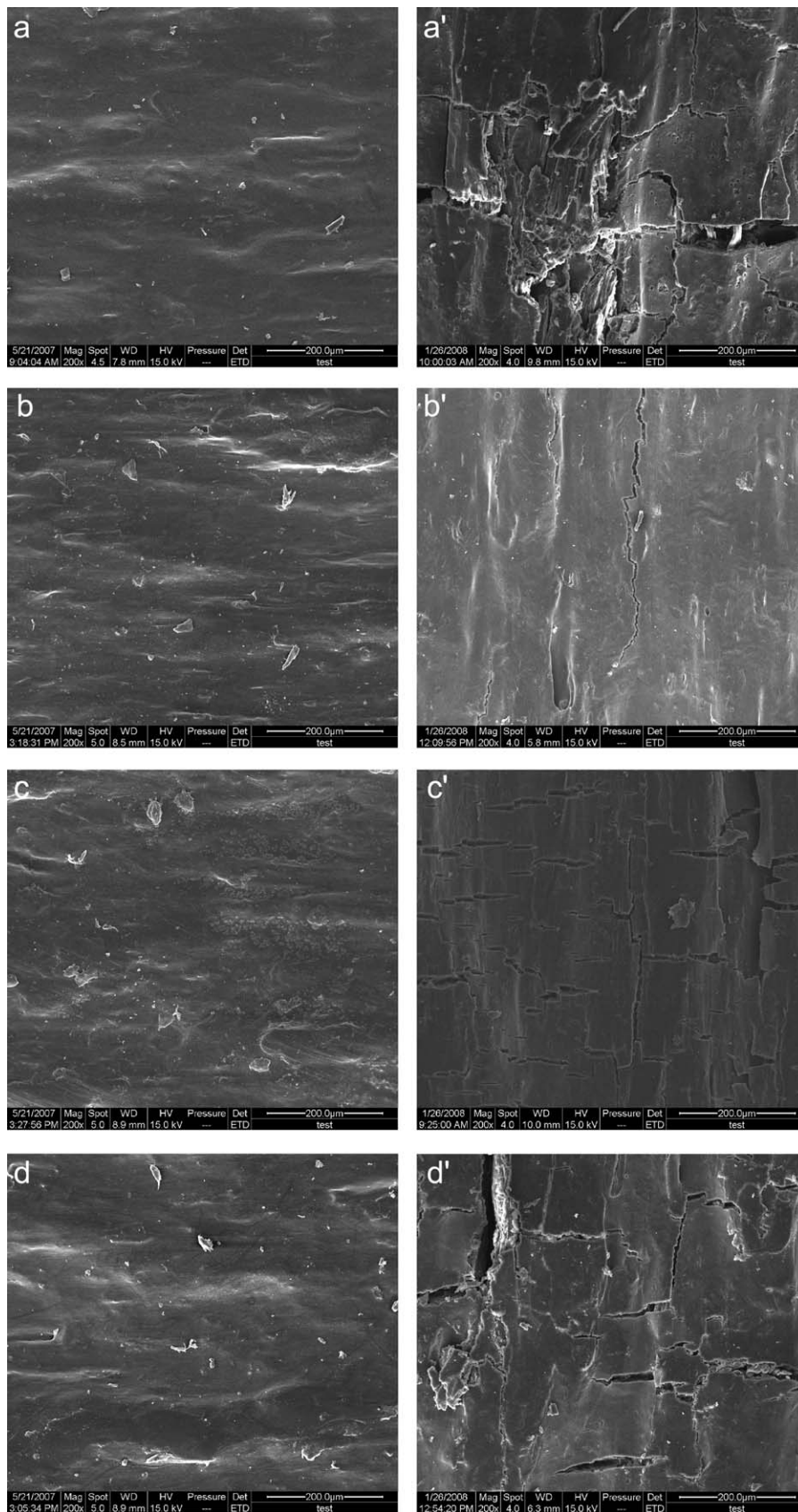


Figure 1 SEM images of WF/HDPE composites before and after UV weathering. (a) WF/HDPE before weathering. (a') WF/HDPE after weathering. (b) WF/HDPE with 2% carbon black before weathering. (b') WF/HDPE with 2% carbon black after weathering. (c) WF/HDPE with 2% colcothar before weathering. (c') WF/HDPE with 2% colcothar after weathering. (d) WF/HDPE with 2% titanium dioxide before weathering. (d') WF/HDPE with 2% titanium dioxide after weathering.

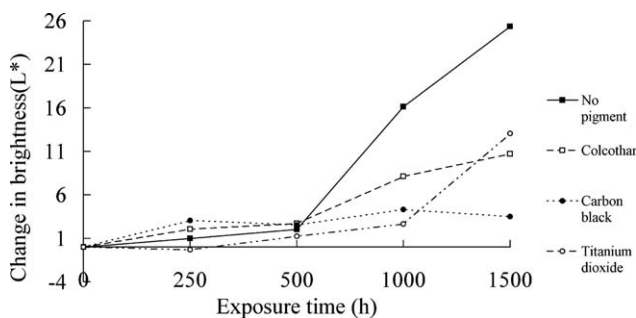


Figure 2 Change in brightness of control and pigmented WF/HDPE composites after accelerated UV weathering.

$$\text{Wood index} = \frac{I_{1056}}{I_{2912}} (100)$$

where I denotes the peak intensity. The peak intensity was normalized to the peak at 2912 cm^{-1} , which corresponds to alkane C—H stretching vibrations of methylene ($-\text{CH}_2-$) groups. This peak was chosen as a reference because it changed the least during weathering.

FTIR was also used to determine the intensity of the C=C peak at 1506 cm^{-1} , which corresponds to stretching of aromatic groups in lignin, as described by Muasher and Sain.^{13,17,18} The peak around 1630 cm^{-1} is the characteristic absorption of conjugated carbonyl group C=O of lignin in WF.¹⁵ The lignin index was calculated in the same way as the wood index but at 1630 cm^{-1} instead of 1056 cm^{-1} .

$$\text{Lignin index} = \frac{I_{1630}}{I_{2912}} (100)$$

In addition, FTIR was also used to measure crystallinity of HDPE using the method described by Zerbi et al.¹⁹ The doublet peaks roughly observed at $1474\text{--}1464\text{ cm}^{-1}$ and $730\text{--}720\text{ cm}^{-1}$ correspond to polyethylene crystalline content (1474 and 730 cm^{-1}) and amorphous content (1464 and 720 cm^{-1}). The percentage crystallinity was calculated according to the following equation:

$$X = 100 - \frac{(1 - I_a/I_b)/1.233}{1 + I_a/I_b} (100)$$

where I_a and I_b can be derived from the bands at either 1474 and 1464 cm^{-1} or 730 and 720 cm^{-1} , respectively.¹⁹ Colom et al. determined that the bands at 730 and 720 cm^{-1} were the most appropriate to study because a peak from cellulose fibers at 1430 cm^{-1} interferes with the 1474 and 1464 cm^{-1} peaks.¹² Using the bands at 1474 and 1464 cm^{-1} , determination of crystallinity leads to unreliable results because these bands are asymmetric. In the work reported here, crystallinity was calculated

using the doublet peaks at 730 and 720 cm^{-1} , respectively.⁸

The FTIR spectra for control WF/HDPE composites are clearly different before and after accelerated UV weathering. The peak at $1700\text{--}1750\text{ cm}^{-1}$ corresponding to C=O stretching increased in intensity after weathering for 250 h (Fig. 4), indicating that surface oxidation occurred in the first 250 h of exposure. In addition, crystallinity changes in the samples reflected structural changes in the matrix after weathering. Changes in the carbonyl index and crystallinity are shown in Figures 5 and 6.

The peak at 1056 cm^{-1} is associated with C—O stretching in cellulose and hemicellulose.^{12,18–20} In this study, the intensity of the peak at 1056 cm^{-1} was very high for control samples before weathering and significantly decreased after UV weathering for 1500 h (Fig. 4), indicating a loss of cellulose and hemicellulose at the composite surface. The peak around $1608\text{--}1630\text{ cm}^{-1}$ and 1507 cm^{-1} attributed to aromatic ring framework stretching in lignin disappeared after UV exposure for 250 h (Fig. 4), indicating photodegradation of the aromatic lignin structure. Changes in the wood index and lignin index are shown in Figures 7 and 8.

Carbonyl group formation

The carbonyl index of pigmented WF/HDPE composites was higher than that of the control samples before weathering (Fig. 5). The addition of pigments introduced various metal ions into the composites. These metal ions (especially ferric ions) can serve as efficient catalysts for the thermooxidative degradation of the composites²⁰ and an increase in oxidation may be expected during extrusion. Carbon black itself has carbonyl group, resulted in the higher carbonyl index of the corresponding composite.

TABLE II
Peak Wavenumbers for FTIR Analysis and the Corresponding Functional Groups and Their Vibration Type^a

Wavenumber (cm^{-1})	Functional group	Vibration
2917 or 2850	$-\text{CH}_2-$	C—H stretching
1700–1750	R(C=O)OH	C=O stretching
1634	C=O (conjugated)	C=O stretching conjugated with benzene ring
1506	aromatic ring	stretching of aromatic ring framework
1470 or 1460	$-\text{CH}_2-$	C—H in-plane deformation
1050–1060	C—O(H)	C—O stretching
730	$-\text{CH}_2-$	C—H rocking (crystalline)
720	$-\text{CH}_2-$	C—H rocking (amorphous)

^a Sources: Refs. 11–15 and 17–20.

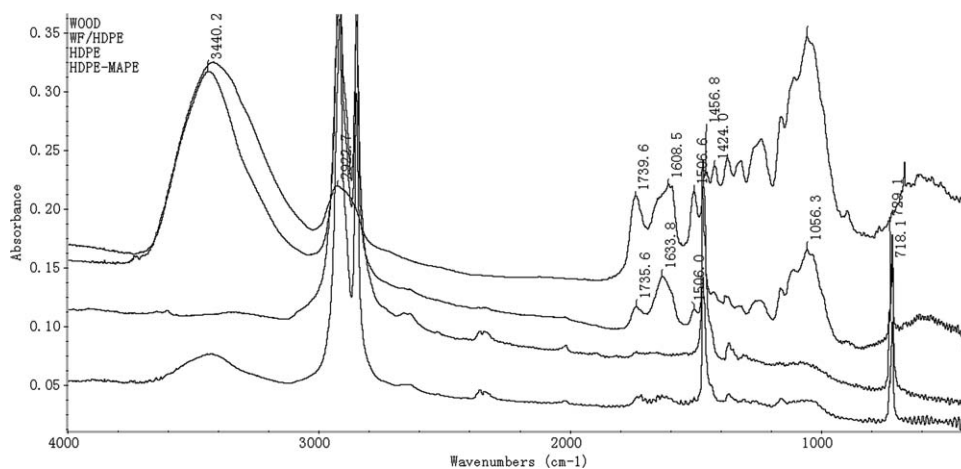


Figure 3 FTIR spectrum of wood-flour, WF/HDPE, HDPE, and HDPE-MAPE.

The carbonyl index of all samples increased significantly in the first 250 h of exposure (Fig. 5). The increase in carbonyl group index for polyethylene after weathering is known to be proportional to the number of chain scissions that occur in the polyethylene.^{8–10} Therefore, the results indicate that chain scission may have occurred immediately upon exposure and that the number of chain scissions increased with the exposure time. At the same time, chain scission decreases the density of entanglements in the amorphous phase, and allows shorter molecules to migrate to the sample surface,^{9,10} which may result in WPC lightening. However, the changes in carbonyl index of samples containing pigments were less than that of samples without pigment in the first 250 h of exposing, and samples containing carbon black exhibited the lowest change in carbonyl index of all pigmented samples in the first 250 h of exposing; the carbonyl index of all samples did not increase significantly from 250 h to 1000 h exposure, and then sharply decreased after

1000 h exposure. The decrease in carbonyl index of the control samples was more significant than that of samples containing pigments, and the decrease magnitude of the sample containing carbon black was the least. These results demonstrate that pigments can effectively prevent WF/HDPE oxidation due to UV exposure. The carbon black may shield more UV-light than other pigments, so carbon black was the most effective in protecting WF/HDPE composites against UV light and thus oxidation.

The results obtained in this study that the carbonyl index of samples decreased after 1000 h exposure is consistent with that of James et al.¹¹ They also found that the carbonyl of WPC increased in the initial stage of UV weathering, and finally decreased after exposing for certain duration. SEM showed that weathering caused more severe cracks and more fractured wood particles emerged on the surface of control samples than that of colored samples. Fractured and loose wood particles might be washed possibly away during condensation cycle,

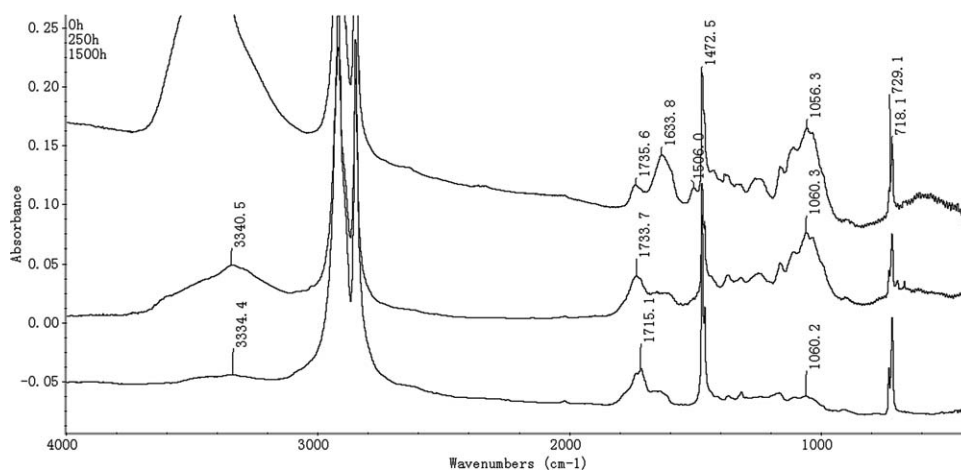


Figure 4 FTIR spectra of control WF/HDPE composites before and after weathering.

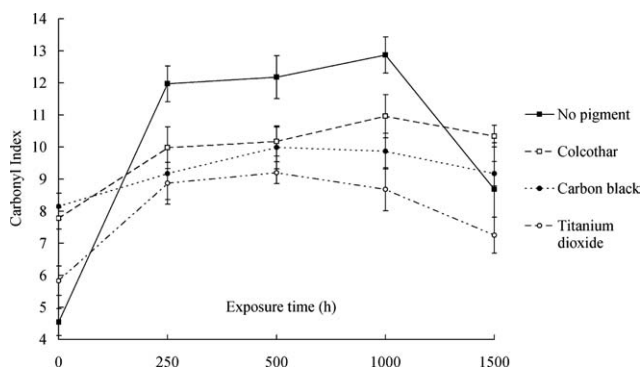


Figure 5 Change in the carbonyl index of control and pigmented WF/HDPE composites after accelerated UV weathering. Each data point represents average of five samples; error bars represent one standard deviation.

which decreased the trace of degraded wood and plastic on the outer surface, resulted in a decrease in the carbonyl index of samples after 1000 h exposure.

Crystallinity changes of HDPE

Figure 6 shows the percentage crystallinity for all WF/HDPE samples. The crystallinity of pigmented WF/HDPE composites was higher than that of the control sample before weathering. Pigment addition led to more oxidation during the manufacture of composites,²⁰ which may result in chain scission in polyethylene occurred and crystallinity increased.

The crystallinity of the HDPE matrix in the control and colcothar samples increased with the exposure time up to 500 h, and then decreased there after. However, the HDPE crystallinity of samples containing carbon black or titanium dioxide increased with the exposure time up to 250 h and decreased there after. Increases in matrix crystallinity can occur if chain scission occurs. Then shorter and more mobile chains recrystallize in the amorphous phase of the polymer. Therefore, an increase in crystallinity is another indication of chain scission in polyethylene during photodegradation.^{8,9,22} Hamid and Amin

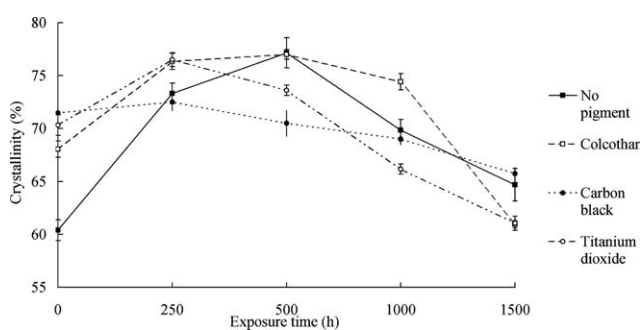


Figure 6 Change in crystallinity of control and pigmented WF/HDPE composites after accelerated UV weathering. Each data point represents average of five samples; error bars represent one standard deviation.

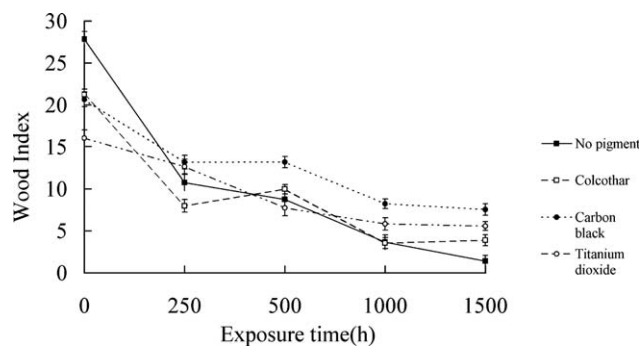


Figure 7 Change in the wood index of control and pigmented WF/HDPE composites after accelerated UV weathering. Each data point represents average of five samples; error bars represent one standard deviation.

studied both natural and accelerated weathering of low-density polyethylene.²³ They concluded that crosslinking and chain scission reactions occur simultaneously. However, during the initial stages of exposure of WF/HDPE composites to accelerated weathering, crosslinking in the matrix does not predominate. It is possible that WF particles physically hinder crosslinking, which would allow for more chain scission and a corresponding increase in crystallinity.⁸⁻¹⁰ Therefore, the increase in crystallinity indicates that the HDPE matrix in all WF/HDPE composites underwent chain scission on exposure. As evidenced by the increase in carbonyl groups, chain scission in the HDPE matrix eventually affected linking molecules, resulting in a breakdown of crystallization and an eventual decrease in crystallinity.^{8-10,12,24}

However, changes in crystallinity differed for the formulations with increasing exposure. The lowest change in crystallinity before and after weathering was observed for samples containing carbon black, indicating that this pigment was more effective than the others in shielding WF/HDPE from UV radiation and thus protecting against photodegradation, in agreement with the previous results.

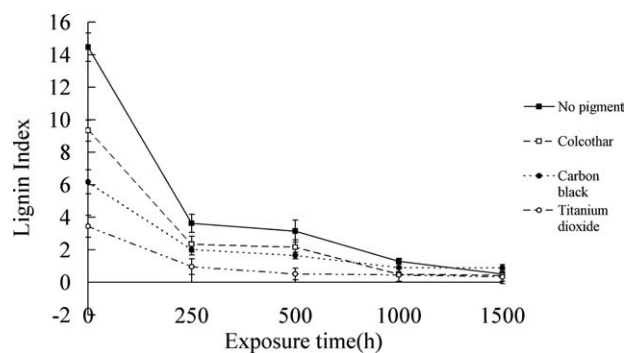


Figure 8 Change in the lignin index of control and pigmented WF/HDPE composites after accelerated UV weathering. Each data point represents average of five samples; error bars represent one standard deviation.

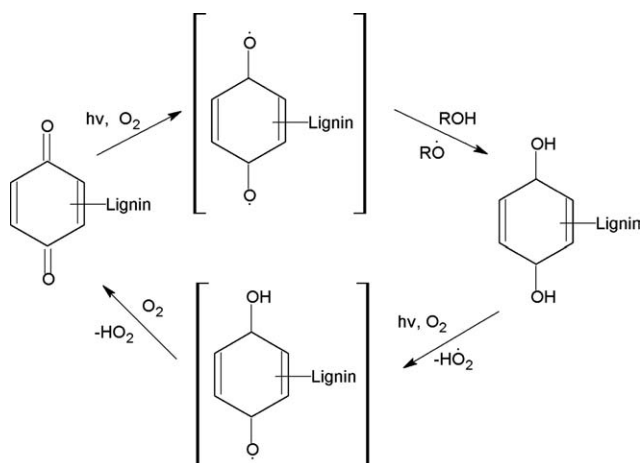


Figure 9 Scheme of phenoxyl quinone redox cycle.

Changes in the wood index

The wood and lignin indexes of pigmented WF/HDPE composites were lower than that of the uncolored samples before weathering (Figs. 7 and 8). We found that the pigment addition slowed down the extrusion rate and compressive stress inside increased by about 3 MPa during the extrusion. In addition, the addition of pigments introduced various metal ions into the composites. These metal ions can serve as efficient catalysts for the thermo-oxidative degradation of the composites.²⁰ All of these may lead to more oxidation, which decreased the wood index and the lignin index, and increased the crystallinity of HDPE and the carbonyl index of composites.

It has been reported^{25,26} that photodegradation of wood can be attributed to the degradation of its components, namely, cellulose, hemicellulose, lignin, and extractives. Thus, changes in the wood index and lignin index can be considered as indications of photodegradation. The wood index of the composites decreased after weathering for 1500 h (Fig. 7), indicating the occurrence of WF photodegradation on the composite surface. It is very likely that weathering caused microcracks on the surface of WF/HDPE composites, which would allow more UV radiation and moisture to enter the interior of WF/HDPE composites, resulting in photodegradation of cellulose and lignin.¹⁰

The wood indexes of all pigmented samples had no significant difference between each other after weathering for 1500 h, as they were higher than that of unpigmented samples. In other words, the change in wood index of unpigmented composites was the greatest during weathering. It was likely that the inorganic pigments could shield more UV-light, so less radiation reaches into the composites board. Thus, pigment can provide more effective protection against microcrack formation and WF photodegradation at the composite surface.

Changes in the lignin index

Figure 8 shows the changes in lignin index for all WF/HDPE samples during accelerated UV weathering. The lignin index decreased with increasing exposure time for all composite samples. The decrease in lignin index confirms that WF photodegradation occurred on the composite surface after weathering. The greatest decrease in lignin index occurred in the first 250 h of exposure for all samples, indicating that lignin is very sensitive to UV light and is degraded immediately under UV irradiation. Lignin degradation eventually leads to the formation of chromophore functional groups such as carboxylic acids, quinones, and hydroperoxy radicals, which are the main cause of discoloration in wood^{25,26} (Fig. 9). This is consistent with FTIR observations that the largest increases in carbonyl index occurred in the first 250 h of exposure. However, hydroquinones and paraquinones form a redox couple.^{13,27,28} Under UV irradiation, the process begins with the hydroquinone oxidation to form paraquinones (chromophore structures), which are further reduced to hydroquinones as the cycle is repeated. Hydroquinones induce WF photobleaching and, therefore, the increases in L^* is very large after 500 h of exposure. The lignin index of all samples had no significant difference between each other after weathering for 1500 h. This indicated that pigments can not effectively prevent lignin photodegradation because of its sensitivity to UV light.

Changes in element content and valence state on composites surface

The results of surface element analysis of WF/HDPE before and after UV weathering by XPS are listed in Table III. The main elements detected were oxygen and carbon. The O/C atomic ratio was calculated as an indication of surface oxidation. XPS data listed in Table III shows an increase in the total number of oxygenated carbon bonds. As a result, after 1500 h of weathering the O/C ratio increased for both the control sample and carbon black samples, indicating that the sample surface had oxidized.

The C1s peak was separated by deconvolution into four sub-peaks, C₁, C₂, C₃, and C₄. The theoretical binding energy and corresponding bond type are shown in Table I. The C₁ peak does not correspond to a C—O bond, whereas the C₂, C₃, and C₄ peaks do. The ratio of oxidized to unoxidized carbon (C_{ox}/C_{unox}) was also calculated:

$$C_{ox}/C_{unox} = \frac{C_{oxidized}}{C_{unoxidized}} = \frac{C_2 + C_3 + C_4}{C_1}$$

A decrease in the C₁ peak intensity indicates a decrease in the concentration of unoxidized carbon atoms. Increases in C₂ and C₃ were observed after

TABLE III
Relative Quantities of Various Carbon–Oxygen Bonds in the Samples of Control and WF/HDPE Containing Carbon Black Determined by XPS

	C1	C2	C3	C4	O1	O2	O/C	C _{ox/unox}
Carbon black								
Unweathered	78.08	5.81	3.44	2.15	6.82	3.7	0.118	0.146
Weathered for 1500 h	69.02	8.93	3.81	1.59	7.31	9.35	0.20	0.208
Control sample								
Unweathered	74.58	6.33	3.26	1.83	6.94	7.06	0.163	0.153
Weathered for 1500 h	50.64	9.54	3.92	1.88	10.99	23.03	0.516	0.303

weathering. On the other hand, weathering significantly increased the C_{ox/unox} ratio for both the control sample and carbon black composites (Table III), implying that significant surface oxidation occurred after 1500 h of exposure. The XPS results are consistent with the FTIR results.

Stark and Matuana^{8,10} found that weathering significantly increased the C_{ox/unox} ratio for both neat HDPE and WF/HDPE composites, proving that substantial surface oxidation occurred after 2000 h of exposure. The increase in C_{ox/unox} ratio for both neat HDPE and WF/HDPE composites appears to be mainly due to an increase in hydroxyl groups (i.e., increase in C₂). In addition, surface oxidation due to weathering was more pronounced for WF/HDPE composite samples than for pure HDPE samples. The C_{ox/unox} ratio increased dramatically for WF/HDPE composites after weathering (80% increase compared with 5% for pure HDPE samples), suggesting that WF addition to the HDPE matrix accelerated surface photo-oxidation.

CONCLUSIONS

XPS analysis revealed that surface oxidation of samples occurred after UV exposure. WF/HDPE composites without pigment showed surface discoloration as a consequence of extensive chemical degradation involving chain scission reactions and the formation of carboxyl groups after UV weathering. Samples containing pigments exhibited less deterioration, less surface discoloration and showed a lower change in carbonyl index than the control with increasing exposure time.

Surface cracks were apparent for all WF/HDPE composites, reflecting significant degradation after accelerated UV aging. However, cracks in the HDPE matrix appeared to be less severe for composites containing pigment than for those without pigment. Pigments can protect the polyethylene matrix of WF/HDPE composites from UV degradation to a certain extent, and carbon black was more effective than the other pigments. However, pigment did not prevent lignin degradation in the WF/HDPE composites since lignin is very sensitive to UV light. Carbon black had a positive effect on color stability.

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