Effects of Carbon Black and Titanium Dioxide on Ultraviolet Weathering of Wood Flour-HDPE/Lumber Composites Using Multi-phase Co-extrusion Technology

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A new type of wood-plastic/lumber composite (WPLC) was fabricated with laminated veneer lumber as a core, and the traditional wood-plastic composite (WPC) as a shell layer using multi-phase co-extrusion technology. This WPLC was used to manufacture a window frame, and the effects of inorganic pigments (carbon black (CB), titanium dioxide (TiO₂), and their mixtures) on the decorative effect and ultraviolet (UV) weathering performance of the shell layer of the window frame were investigated. Weathering variables included UV irradiation duration and water spraying cycles for up to 6000 h. The surface color was analyzed by spectrophotometry during weathering. In addition, a scanning electron microscopy analysis and Fourier transform infrared spectroscopy analyzed the weathering properties of the WPLC shell layer. The results showed that (1) different decorative effects (white, grey, and black color) of the window frames were achieved by incorporating CB, TiO₂, and their mixture; (2) the composites incorporated with CB and/or TiO₂ exhibited less discoloration and fewer surface cracks; (3) the composites with CB and TiO₂ showed a better photo-stability than those with a UV stabilizer (UV326). The overall color change (ΔE) of the composites incorporated with UV326, TiO₂, and CB was 20.0, 11.7, and 10.8, respectively, after 3000 h of weathering; and (4) a combination of CB and TiO₂ showed a synergistic effect on alleviating the photo-oxidation process of the WPC shell layers, which confirmed its UV-shielding effect.

Keywords: Wood-plastic/lumber composites; Window frame; Co-extrusion; Accelerated weathering; Carbon black; Titanium dioxide

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INTRODUCTION

Windows are indispensable functional components in construction. The coverage of windows usually accounts for more than 15% of the whole construction, and it is the main source of construction energy and materials consumption. Accordingly, it is very important that the windows are energy-efficient and their material and construction ensure long life cycles. Moreover, windows are decorative and also serve as maintenance structures; thus, one of the most important development trends for windows is to meet the aesthetic and personalized demand of consumers (such as color, appearance, and texture). Currently, the main window manufacturing materials remain a significant challenge. For instance, aluminum alloy is a high-energy consumption material with high emissions during production, and windows made of this material have poor thermal performance and
sound insulation properties. Polyvinyl chloride (PVC) plastic material deforms easily due to creep; thus, windows made of such material deform easily, which will decrease the thermal insulation property and wind-resistant performance of the windows. Additionally, its disposal causes severe environmental pollution if not collected selectively, and not recycled. Although solid wood windows have advantages in thermal insulation and a decorative effect, they have a relatively short service life due to their poor decay resistance and susceptibility to cracking. Moreover, the maintenance cost of solid wood windows is high, and high-quality wood resource is limited in China. In summary, finding and producing new materials to make window frames is demanded by the market and has important academic research value.

Wood-plastic composites (WPCs) made from lignocellulosic fibers, thermoplastics, and additives have experienced significant market growth in several applications, including interior components in the automotive industry, door and window frames, decking, cladding, and fencing (Homkhiew et al. 2014). Windows made of WPCs show prominent advantages of being green, energy-efficient, and environmentally friendly (Defosse 1999), but the ease of cracking and creep still remain problematic in such windows due to their hollow structure (Bledzki and Faruk 2004). Therefore, WPC windows are mainly used in low-rise buildings, and sometimes are used in high-rise buildings only if the windows are protected by a steel structure that can improve the wind-load resistance performance of the windows.

Wood-plastic/lumber composites (WPLCs) fabricated by multi-phase co-extrusion technology use solid lumber that is well-proportioned and stable, such as laminated veneer lumber (LVL), integrated timber, as well as scrimber, to act as the core material, and they use WPCs as the shell layer to coat the surface (Figs. 1a and 1b). This material perfectly combines the advantages of the solid lumber and WPCs, using solid lumber to achieve mechanical strength support and WPCs to protect the vulnerable solid lumber. Accordingly, such materials not only possess excellent mechanical strength and stiffness properties, but they can also greatly decrease the occurrence of creep during service, and after decay and wear damage caused by the changes of humidity, temperature, and light in the environment (Wang et al. 2014, 2015, 2016). The WPLC is qualified to be used as a fine window frame material, which allows this material to be used in window products.

![Fig. 1. (a) Schematic of window frame profiles fabricated using WPLC, (b) match schematic of a WPLC window frame and sash, and (c) picture of a window fabricated using WPLC profiles in the authors’ lab](image-url)
Although WPCs have potential application in the fabrication of windows, their decorative effect and durability performance are critical issues that should be considered for their practical application (Azwa et al. 2013). The WPCs are made of polymers and wood flour (WF), which experience photo-degradation upon exposure to ultraviolet (UV) light (Peng et al. 2014a; Shen et al. 2016). The outdoor applications expose windows to a range of harsh environments (e.g., humidity, basic, acid and alkaline solutions, temperature, freeze-thaw, thermal cycles, UV light, etc.), which can cause discoloration, chalking, and strength weakening of the WPCs shell layer (Hung et al. 2012). Inorganic pigments, such as titanium dioxide (TiO₂) and carbon black (CB) have received much attention in recent years due to their UV absorption ability and effect on color stability of composites (Liu and Horrocks 2002; Du et al. 2010; Deka and Maji 2011; Butylina et al. 2015). Additionally, different mixing ratios of TiO₂ and CB can be used to make windows of different colors.

In this study, WPLC window frame profiles were fabricated. To achieve both the aging resistance and a decorative effect of the WPCs shell layer, this study used nano-CB and rutile nano-TiO₂ as colorant and anti-UV agent. The UV-absorber UV326 is frequently used as an anti-UV agent in the WPC industry, and it was also applied in this study as a reference. The WPCs shell layers were exposed to alternating cycles of UV irradiation and water spraying in an accelerated weathering chamber for 6000 h. The surface characteristics were evaluated by colorimetric measurements, scanning electron microscopy (SEM) analysis, and Fourier transform infrared (FT-IR) spectroscopy.

**EXPERIMENTAL**

**Materials**

High-density polyethylene (HDPE) pellets (5000S) were purchased from Daqing Petrochemical Co., Daqing, China, with a density of 0.954 g cm⁻³ and a melt flow index of 0.7 g/10 min (190 °C, 2.16 kg according to ASTM D1238 (2004)). Wood flour (WF) was prepared from poplar (Populus euramericana cv. 'I-214') veneer in a hammer mill to pass through 80- to 100-mesh sieves. Laminated veneer lumber (LVL) made from poplar (Populus euramericana cv. 'I-214') veneer was provided by Xuzhou Shenghe Wood Co., Ltd., Jiangsu, China. It had a dimension (L × W × H) of 2000 mm × 74 mm × 35 mm, a density of 0.59 g cm⁻³, and a moisture content of 9% to 10%. Maleic anhydride grafted polyethylene (MAPE; type 9804, Shanghai Sunny New Technology Development Co., Ltd., Shanghai, China) with a grafting ratio of 0.9% was used as a compatibilizer. The lubricants (Lub) used were paraffin, polyethylene wax, ester stearate, and calcium stearate at a weight ratio of 1:1:1:1. Rutile TiO₂ (R-103) was purchased from DuPont Co., Ltd., Wilmington, DE, USA. Carbon black (CB; BP-2000) with particle size 12 nm was obtained from Cabot Chem., Corp., Boston, MA, USA. The TiO₂ and CB were both used as colorant and anti-UV agent. The 2-(2-hydroxy-3-tert-butyl-5-methylphenyl)-5-chlorobenzotriazole (UV326), which was used as a UV absorber, was produced by BASF Chemical Co., Ltd., Tianjin, China. The calcium carbonate (CaCO₃; 10 µm, white powder) was purchased from Shanghai Calcium Carbonate Co., Ltd., Shanghai, China.

**Preparation of composites**

Beforehand, the WF was dried 12 h at 103 °C to remove moisture. Then, the dried WF, HDPE matrix, MAPE, lubricants, and other additives were mixed at a specific ratio.
(Table 1) in a high-speed mixer for 8 min. The mixture was melt-blended and pelletized into WPCs pellets using a co-rotating twin-screw extruder (SWMSZ-2, SKY WIN Technology Co., Ltd., Nanjing, China) with a screw diameter of 65 mm and an L/d ratio of 48. The corresponding temperatures in the extruder barrel were 145 °C to 170 °C from the feeding to die zone and the screw rotating speed was fixed at 100 rpm. The WPLC window frame profiles were produced using laboratory-designed co-extrusion equipment. The major parts of the co-extrusion equipment are a 65 mm/132 mm counter-rotating conical twin screw extruder (SWMSX-3, SKY WIN Technology Co., Ltd., Nanjing, China), a laboratory-designed chamber and die, and a supplementary feeding device for solid timber. The processing conditions for co-extrusion were as follows: (1) temperature profiles: 145 °C to 170 °C; (2) screw rotating speed: 60 rpm; and (3) feeding speed of LVL: 20 cm min⁻¹. The WPCs shell layers were peeled from the WPLC profiles for accelerated weathering. The surfaces of the WPCs shell layers were sanded with 200-mesh sand paper to remove the HDPE layer. All samples tested were sanded.

**Table 1. Wood-plastic Composite Formulations (wt.%)**

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>WF</th>
<th>HDPE</th>
<th>CaCO₃</th>
<th>MAPE</th>
<th>Lub</th>
<th>UV326</th>
<th>TiO₂</th>
<th>CB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ctrl</td>
<td>55.6</td>
<td>33.3</td>
<td>4.6</td>
<td>3.7</td>
<td>2.8</td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>WPC-U</td>
<td>55.6</td>
<td>33.3</td>
<td>4.6</td>
<td>3.7</td>
<td>2.8</td>
<td>0.5⁴</td>
<td></td>
<td></td>
</tr>
<tr>
<td>WPC-T</td>
<td>55.6</td>
<td>33.3</td>
<td>4.6</td>
<td>3.7</td>
<td>2.8</td>
<td>5⁴</td>
<td></td>
<td></td>
</tr>
<tr>
<td>WPC-C</td>
<td>55.6</td>
<td>33.3</td>
<td>4.6</td>
<td>3.7</td>
<td>2.8</td>
<td>0.5⁴</td>
<td></td>
<td></td>
</tr>
<tr>
<td>WPC-T-C</td>
<td>55.6</td>
<td>33.3</td>
<td>4.6</td>
<td>3.7</td>
<td>2.8</td>
<td>5⁴</td>
<td>0.5⁴</td>
<td></td>
</tr>
</tbody>
</table>

* a: the weight percent of UV326, TiO₂, and CB was based on the total weight of WF, HDPE, CaCO₃, MAPE, and Lub

**Weathering**

Accelerated weathering was conducted in a Q-UV Weatherometer (Q-Lab Corp., Westlake, OH, USA) that simulates the damage similar to sunlight, rain, and dew. The rectangular test samples measuring 80 mm × 13 mm × 4 mm were mounted on aluminum fixtures and subjected to accelerated UV weathering via 340-nm fluorescent UV lamps (UV-B lamps) with a UV irradiation intensity of 1.55 W m⁻². Tests were conducted according to the procedure outlined in the ASTM G0154 (2004) and included a 12 h cycle that consisted of 8 h irradiation at 60 °C, 15 min water spray, and 3 h 45 min condensation at 50 °C. The above process was repeated 500 times, giving a total of 6000 h of accumulated exposure for each group. Weathered samples were removed for analysis after 250, 500, 1000, 2000, 3000, 4000, 5000, and 6000 h of exposure.

**Color measurements**

The surface color of the samples was measured with a Konica Minolta CM 2300d spectrophotometer (Minolta Konica, Tokyo, Japan) according to the CIELab color system at 23 °C and 65% relative humidity. The lightness (L*) and chromaticity coordinates (a* and b*) were measured for five replicate samples. The L* represents the lightness coordinate and varies from 100 (white) to 0 (dark). The a* represents the red (+a*) to green (−a*) coordinate, and b* represents the yellow (+b*) to blue (−b*) coordinate. The total color changes or discolorations (ΔE) of the un-weathered and weathered composite specimens were calculated by Eq. 1,

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

where subscript 1 denotes the values of the un-weathered composite specimens, and subscript 2 denotes the values of the weathered composite specimens. An increase in $L^*$ means that the sample has lightened or faded (i.e., positive $\Delta L^*$ for lightening and negative $\Delta L^*$ for darkening). Similarly, a positive $\Delta a^*$ represents a color shift toward red, and a negative $\Delta a^*$ represents a color shift toward green. A positive $\Delta b^*$ represents a color shift toward yellow, and a negative $\Delta b^*$ represents a color shift toward blue.

**Scanning electron microscopy (SEM)**

The surfaces of the samples were sputter-coated with gold (JEOL, JCS 1100, Tokyo, Japan) and analyzed by a scanning electron microscope (QuanTa200, FEI Company, Hillsboro, OR, USA) at a working distance of approximately 25 mm with a voltage of 15 kV and a probe current of $6 \times 10^{-10}$ A.

**Fourier transform infrared (FT-IR) spectroscopy analysis**

The FT-IR spectra were recorded using a Nicolet 6700 spectrometer (Thermo Fisher Scientific Inc., Madison, WI, USA) equipped with smart ATR accessory with diamond crystal. Each spectrum was the result of 40 scans with 4 cm$^{-1}$ resolution. Spectra were recorded in the standard Mid-IR region 4000 cm$^{-1}$ to 650 cm$^{-1}$. The peak intensities were normalized using the peak at 2912 cm$^{-2}$, which corresponds to alkane CH stretching vibrations of the methylene groups. This peak was chosen as a reference peak because it changed the least during weathering.

**RESULTS AND DISCUSSION**

**Colorimetric Analysis**

The visual appearance of the un-weathered composites (a through e) and weathered composites after 6000 h (f through j) are presented in Fig. 2. The surface color of the reference samples (Ctrl) without addition of any pigment (Fig. 2a) and samples containing UV absorber UV326 (Fig. 2b), almost retained the original yellow-brown color. For the WPC samples with 5% rutile nano-TiO$_2$, the surface color became a light tawny, which indicated an obvious covering effect of TiO$_2$ relative to the surface color of the WPCs.

![Fig. 2. Visual appearance of the un-weathered composites (a-e) and weathered composites after 6000 h (f-j): (a) and (f) Ctrl, (b) and (g) WPC-U, (c) and (h) WPC-T, (d) and (i) WPC-C, and (e) and (j) WPC-T-C](image)
The surface color of the WPCs with the addition of 0.5% CB was black, which showed that the CB had a high coloring efficiency. The WPCs had the color of medium grey when the grey compound colorants, composed of 5% TiO$_2$ and 0.5% CB, were added, and indicated that the coloring ability of CB was stronger than that of TiO$_2$.

The above results indicated that using TiO$_2$ and CB as a colorant could produce WPCs with white, grey, and black color, and the grey level of WPCs was effectively controlled by adjusting the amount of CB and TiO$_2$ added. However, the inherent colors of wood flour and other ingredients had an influence on the color of the produced WPCs, and their effect on light colored WPCs was more noticeable. Therefore, more attention should be paid to inspect and control the color of the raw materials when light colored WPCs are expected and discoloration of the raw materials maybe necessary, according to the requirement of the final products’ color.

The degree of aging of the Ctrl was most obvious after 6000 h of exposure (Fig. 2f). The damage appeared to be very serious, such that the original color could not be identified due to the discoloration, and the original appearance could not be ascertained due to the cracked fragments formed on the surface. The degree of aging of the samples that contained UV326 was slightly lower than that of the control (Fig. 2g), which indicated that the addition of UV326, to some extent, prevented aging. However, their original appearance still could not be ascertained, because the samples were discolored and turned white, and there were slightly cracked fragments on the surface. For the samples with the addition of 5% TiO$_2$, their degree of aging was also slightly lower than that of the control samples, and they also had lost the original color and morphology (Fig. 2h).

The discoloration of the weathered samples could be attributed to the photo-oxidation of lignin (Muasher and Sain 2006; Peng et al. 2014b). Actually, UV radiation induces photo-oxidation, especially that of lignin, which is the wood flour component more sensitive to UV light due to the presence of chromophoric groups in its structure (Peng et al. 2014b) linked to the surface bleaching. Two reactions may occur. Initially, a chain scission of lignin macromolecules can lead to the formation of paraquinonic structures causing a yellowing of WPCs. Then, paraquinones can be reduced to hydroquinones, which give a white color to the composites (photo-bleaching). This discoloration of WPCs from brown to chalky white has been observed for wood flour polypropylene composites (Peng et al. 2014b). With the addition of 0.5% CB into WPCs, their hue changed after weathering, and the color changed to a cool color and deepened (Fig. 2i). This shows that the addition of a small amount of CB had a remarkable effect on the aging resistance of WPCs. For the samples that contained the mixture of 5% TiO$_2$ and 0.5% CB, their color deepened after weathering.

The above results showed that the WPCs that contained CB retained the original morphology and color after 6000 h accelerated UV weathering. Therefore, it is reasonable to select CB as a colorant and anti-aging agent for WPCs that are intended to be used as outdoor building materials in an environment with light exposure and long periods of rain. Moreover, the amount of CB required is much smaller than that of TiO$_2$, so it has the advantage of being less expensive. The price ratio for TiO$_2$ (ordinary size particles) to CB (nano-size particles) used in this research is about 1 to 1.56.

The un-weathered reference composite samples had an initial lightness of 65.9 (Fig. 3a). The addition of TiO$_2$ increased the lightness of the composites to 80.2, while the addition of CB decreased the lightness compared to that of the Ctrl. The samples of composites that contained UV326 had a lightness and color comparable to that of the Ctrl.

In the process of UV weathering, the lightness ($L^*$) of all samples changed with the
increase of the weathering duration, and the most obvious lightness change appeared in the first 250 h (Fig. 3a). This result indicated that under the UV irradiation, the fabricated composites discolored distinctly in the first 250 h of weathering. This was because the scissions of the molecular chain of HDPE occurred immediately due to a photo-degradation reaction, which resulted in a decrease in density of the amorphous regions of HDPE. In addition, short-chain hydrocarbons migrate to the surface and lignin photo-bleaching leads to the change of lightness (Jabarin and Lofgren 1994; Muasher and Sain 2006). The lightness of the Ctrl, WPC-U, and WPC-T increased, while the lightness of WPC-C and WPC-T-C decreased. This meant that the samples with added CB were darkened during weathering. The discoloration rate decreased with the duration of the weathering, and became almost stable after 3000 h.

Both the red-green axis index ($a^*$) and yellow-blue axis index ($b^*$) of WPCs decreased in the early stage of UV irradiation (Figs. 3b and 3c), which meant that the colors of the samples changed from red-yellow to blue-green. The decrease in yellowness ($b^*$) during weathering was attributed to the reduction of paraquinones (chromophoric structures) to hydroquinones, which resulted in photo-bleaching (Butylina et al. 2012). The $a^*$ of all samples tended to be neutral overall after 1000 h of weathering. The $a^*$ and $b^*$ values of the Ctrl, WPC-U, and WPC-T changed remarkably, while the $a^*$ and $b^*$ values of WPC-B and WPC-T-B only changed slightly. The samples that contained both TiO$_2$ and CB were blue-green in all of the UV weathering stages.

The overall color change ($\Delta E$) varied in the formulation of the WPCs. The $\Delta E$ change range of the samples with added UV326 was 9.8, which was smaller than that of the Ctrl (14.5) in the first 250 h of UV weathering. This revealed that the addition of UV326 reduced the photo-degradation rate. However, with the prolongation of the duration of

![Fig. 3. The color parameters the composite surface at different weathering stages (a) $L^*$, (b) $a^*$, (c) $b^*$, and (d) $\Delta E^*$](image-url)
weathering, the $\Delta E$ change range was similar to that of the Ctrl with a similar $\Delta E$ value, and indicated that the photo-stability of UV326 was limited in the long run. The $\Delta E$ of samples that contained inorganic pigments was considerably lower than that of the Ctrl, which indicated that the addition of pigments effectively reduced the lightness change. Additionally, the $\Delta E$ values of WPCs with CB (10.8) were smaller than those of WPCs with TiO$_2$ (11.7) after 3000 h weathering, which showed that CB more effectively protected the composites from discoloration. This might be because the carbon black contains the unique polycyclic aromatic hydrocarbons as well as a hydroxyl group, such as aryl ketone, phenol, quinone, and self-stable free radical, which are structures that have functions in UV shielding, as well as excited state quenching and free radical trapping (Donnett et al. 1993). Accordingly, CB is a highly efficient light stabilizer for a polymer. The results in this study were consistent with the findings of Kiguchi et al. (2007) and Butylina et al. (2012) who studied wood flour-polypropylene composites colored with different colorants, and concluded that darker pigments improve color stability. The composites with a mixture of TiO$_2$ and CB as colorant had a minimal $\Delta E$ of 8.6 after 3000 h weathering, which suggested the existence of a synergistic effect between TiO$_2$ and CB, thereby the ability to resist the effects of ultraviolet light and oxidation was enhanced.

**Surface Morphology of Composites**

The surfaces of the WPCs became rough after sanding, but there was no new defect. The purpose of sanding was to directly analyze the properties of the real material, because the sanded samples are closer to a realistic situation after long-term weathering. For the reference samples, compared with the un-weathered composites (Fig. 4a), obvious micro-cracks on the surface of weathered composites were observed (Fig. 4b) after 250 h of weathering. The main reason for this phenomenon was due to the photo-degradation of HDPE under UV irradiation, which made the long molecular chains break into shorter chains, and micro-cracks appear in the aged HDPE with decreased mechanical properties and micro-cracks appeared under the effect of cohesive force. At the same time, the wood flour inside WPCs expanded and shrank frequently due to the absorption and desorption of water during water spraying, in which the HDPE bore great stress, and the micro-cracks continued to extend in width and depth and became larger (Fig. 4c). The larger cracks helped UV light and water enter into deeper layers, which further accelerated the degradation of HDPE and wood flour, and finally resulted in the serious cracking and peeling on the composite surface.

After 1000 h of weathering, the cracks on the surface of the composites with UV326 were much fewer than those on the Ctrl. This was mainly because the UV326 could absorb a certain amount of UV, and the energy was dissipated in the form of heat. Therefore, UV326 improved the aging resistance of WPCs. Small cracks also appeared on the surfaces of WPCs with the addition of both TiO$_2$ and CB, but the cracks were much smaller than those found on the surface of the Ctrl, which suggested that the addition of colorants improved the aging resistance of WPCs. This was mainly because the colorants could absorb or shield a certain amount of UV irradiation, and resulted in the reduction of the UV irradiation that penetrated into WPCs. This effect thus decreased the degradation of WPCs. The images in Fig. 4 also indicated that the addition of photostabilizers, such as UV326 or inorganic colorants, to the composites could not completely prevent the damage of WPCs surface from the UV irradiation.
The degree of cracking of WPCs with addition of both TiO$_2$ and CB colorants was not severe (Figs. 4n and 4o). This may have been because of the strong UV light-scattering and UV light-absorption capability of rutile TiO$_2$ powder and the UV light-absorption capability of CB. These two colorants had different reaction mechanisms and may have exhibited a synergistic effect, which resulted in the enhancement of oxidation resistance.
caused by UV. The related issues need to be further studied in the future work. The SEM images of aged WPCs with addition of 5% TiO₂ and 0.5% CB at different weathering periods from 250 h to 6000 h are presented in Fig. 5. These images revealed that with the increase of the weathering duration, the small cracks on the surface of the samples increased. However, there was no peeling, and the aging effect of UV light only occurred on the surface of the composites, which showed that the composites that contained CB and TiO₂ had an obvious effect on the long-term resistance to UV-induced aging.

![SEM images of aged WPCs](image)

**Fig. 5.** SEM images of the WPC-T-C surface at different weathering stages: (a) 0 h, (b) 250 h, (c) 500 h, (d) 1000 h, (e) 2000 h, (f) 3000 h, (g) 4000 h, (h) 5000 h, and (i) 6000 h

**Surface Chemistry by FT-IR**

The FT-IR spectra revealed changes in the surface chemistry of the composites during UV-accelerated weathering (Fig. 6). The spectral region from 1670 cm⁻¹ to 1610 cm⁻¹ appeared to be vinyl groups (Soccalingame et al. 2016). In the carbonyl region (1750 cm⁻¹ to 1710 cm⁻¹), a sharp peak was exhibited at 1715 cm⁻¹ with a shoulder peak at 1737 cm⁻¹, which corresponds to hydrogen-bonded carboxylic acids and esters groups, respectively (Stark and Matuana 2004). It is well-known that polyolefin will mainly undergo two chain fracture reactions, including Norrish I and Norrish I, under UV irradiation, producing a carbonyl group and a vinyl group, and the short chain will undergo a cross-linking reaction (Hung et al. 2012). As the exposure time increased, the carbonyl
and ester groups increased at approximately the same rate for all of the composites. The increase in carbonyl and ester group formation for composites after weathering is known to be proportional to the number of chain scissions that occur in the HDPE. However, after more than 2000 h of weathering, the absorption peak did not increase linearly. This may have been because the aging layer peeled off after water spraying, and the inner layer was not exposed by the aging material.

The absorption peaks of the vinyl groups in the range of 1670 cm\(^{-1}\) to 1610 cm\(^{-1}\) were most stable in the 1000 h duration for the WPCs with addition of UV 326 (Fig. 6b), but for those the absorbance peaks clearly rose with the increase of weathering duration. This result showed that UV326 protected the WPC materials well at the initial stage of UV radiation, but afterwards it lost the ability to resist aging due to its own consumption. Because the UV absorber UV 326 is an organic compound, it has limited durability. Thus, in the case of long-term light aging, the protection that it provides may be inadequate.

![Fig. 6. FT-IR spectra of (a) Ctrl, (b) WPC-U, (c) WPC-T, (d) WPC-C, and (e) WPC-T-C at different weathering stages](image)

The absorption peaks of the esters groups in the range of 1670 cm\(^{-1}\) to 1610 cm\(^{-1}\) decreased substantially for the WPCs with the addition of nano-TiO\(_2\) (Fig. 6c). This was because of the strong light-reflection capability of rutile TiO\(_2\). These findings implied that rutile nano-TiO\(_2\) contributed to reduce the photodegradation-induced chain scission of HDPE. After the addition of CB (Fig. 6d), the absorbance peaks of esters groups markedly decreased compared with those of the reference, and this was attributed to the prominent light absorption capability of CB. By compounding TiO\(_2\) and CB (Fig. 6e) as the colorant and anti-UV agent, the surface chemical bonds had few changes after 3000 h of UV-accelerated weathering, and the duration for WPCs to resist UV-accelerated weathering could be prolonged up to 6000 h based on the above analysis of color and surface morphology in this paper. It was far longer than the commonly used 2500 h or the reported 4000 h in other reports, which indicated that WPCs with the addition of this compound coloring system had excellent durability and good prospect for application.

CONCLUSIONS

1. Different decorative effects of the WPLC window frame profiles were obtained by changing the nano-CB to rutile nano-TiO\(_2\) ratio.

2. The composites with inorganic colorants, like nano-CB and rutile nano-TiO\(_2\), exhibited less discoloration and fewer surface cracks. The \(\Delta E\) of the composites incorporated with UV326, TiO\(_2\), and CB was 20.0, 11.7, and 10.8, respectively, after 3000 h of weathering.

3. A combination of nano-CB and rutile nano-TiO\(_2\) exhibited a synergistic effect on retarding the photo-oxidative aging of the WF/HDPE shell layers, which confirmed their UV-shielding effect. These results provided a theoretical reference for developing WPLC windows with better photo-stability.

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