Ultraviolet weathering of WPCs Coextruded with a Clear Cap Layer

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ABSTRACT

This study examined the effect coextruding a clear HDPE cap layer onto HDPE/wood-flour composites has on the discoloration of coextruded composites exposed to accelerated UV tests. Chroma meter, XPS, SEM, and UV vis measurements accounted for the analysis of discoloration and degree of oxidation of both uncapped (control) and coextruded composites before and after UV exposures. Two separate discoloration characteristics occurred in the discoloration of composites. For uncapped WPCs (control), chemical changes due to photooxidation resulted in darkening followed by physical changes, including loss of colored wood components from the surface, as well as increased roughness on the surface, which led to lightening of WPCs. By contrast, because a hydrophobic cap layer prevented the loss of colored components from the surface, coextruding a clear hydrophobic HDPE cap layer over WPCs significantly decreased the discoloration during the weathering process. Photooxidation of wood components at the interface accounted for the discoloration of coextruded WPCs before the failure of cap layer. Moreover, as the cap layer absorbed a specified amount of UV light and reduced oxygen available to interface, it decreased the photooxidation rate at the interface compared to that at the WPCs surface.

1. Introduction

Wood fiber and polymers such as PVC, HDPE, and PP comprise wood-plastic composites (WPCs). The major applications of WPCs in North America include decking, siding, railings, fences, window and door frames, etc. These outdoor applications expose WPCs to moisture, fungi, freeze-thaw actions, and ultraviolet light in sunlight. Since both wood fiber and polymer matrix experience photodegradation upon exposure to ultraviolet light, weathering of WPCs results in severe discoloration and a modest loss of mechanical properties [1-8]. A significant feature of WPCs, aesthetic value, becomes compromised through discoloration, making it a major concern.

Current approaches of improving the weathering resistance of WPCs focus on the bulk of WPCs, i.e., incorporation of additives into the entire product or surface treatment of the wood fiber [2,10,11]. For example, adding photostabilizers and pigments provides protection against discoloration caused by UV radiation. Although adding stabilizer or pigment into the entire composites improves their resistance to photodegradation, weathering primarily occurs at the surface of a material [1-9]. Protecting the WPC surface from weathering would be a cost-effective alternative to protecting the bulk of the material.

Coextrusion is a method available to provide a protective surface on WPCs by manufacturing a multilayered product with different properties at outer and inner layers, thus offering different properties between surface and bulk [12,13]. Encapsulation of WPCs with an HDPE or PVC surface rich cap layer through coextrusion significantly delays the water absorption and improves flexural strength compared to nonencapsulated WPCs [14-18]. Because of water's significance in weathering of WPCs [6,7], coextruding a hydrophobic clear cap layer onto WPCs may retard their discoloration. Coextrusion of a clear cap layer has been shown to be effective at retarding discoloration, but that the mechanism of photodegradation of the composites with a clear cap layer has not been determined [18].

The main aim of this study examined the role coextruding a clear HDPE cap layer onto HDPE/wood-flour composites has on the photo-discoloration of coextruded composites exposed to accelerated weathering tests in order to elucidate the discoloration mechanisms involved in WPCs and assist in developing strategies to reduce the weathering-induced discoloration of WPCs. Particular emphasis focused on exposing both uncapped (control) and coextruded WPCs to accelerated weathering tests and monitoring the surface changes by color measurement, XPS, SEM, and UV-vis measurement.

2. Experimental

2.1. Materials

NOVA Chemicals supplied the neat HDPE (SCLAIR® 19G) used as the cap layer. This polymer (termed as HDPE_{1.2}), in pellet form, had a melt flow index of 1.2 g/10 min and a density of 0.96 g/cm³. Another HDPE (FORTIFLEXTM B53–35H-FLK) obtained from B.P. Solvay Polymers was used as the polymeric matrix for uncapped composites (control) and as the core layer for coextruded composites. This polymer (termed as HDPE_{0.4}), in flake form, had a melt flow index of 0.49 g/10 min and a density of 0.9 g/cm³. Materials for wood flour included the 0.425 mm (40 mesh) maple from American Wood Fibers (Schofield, WI). The wood flour was oven-dried at 105 °C for ~48 h before processing to remove moisture. The lubricant TPW104 (a blend of aliphatic carboxylic

acid salts and mono and diamides) from Struktol® Company (Stow, OH) was used to ease processing and improve the surface quality of composites.

2.2. Compounding and extrusion

A 20-L high intensity mixer (Papenmeier, Type TGAHK20) used for room temperature dry blending of the HDPE $_{0.4}$ matrix, dried wood flour, and lubricant operated for 10 minutes. The formulation of the core layer composites contained 50 % maple flour, 44 % HDPE $_{0.4}$, and 6 % lubricant, based on the total weight of the composites.

Manufacturing of coextruded composites used core layers that contained HDPE $_{0.4}$ /wood-flour composites formed using a 32-mm conical counter rotating twin-screw extruder (C.W. Brabender Instruments, South Hackensack, NJ) with a length-to-diameter ratio of 13:1. The processing temperature profile of the extruder performed at 130/135/135/135 °C from hopper to the coextrusion die and the rotational screw maintained a constant speed at 40 rpm throughout processing. A 19 mm single-screw extruder (C.W. Brabender Instruments, South Hackensack, NJ) with a length-to-diameter ratio of 30:1 produced the neat HDPE with MFI of 1.2 g/10 min (HDPE $_{1.2}$) used as cap layers. The processing temperature profile of this extruder ran at 165/155/145/135 °C from hopper to coextrusion die. The rotational screw maintained a speed set at 2 rpm to produce a thin cap layer (0.20 \pm 0.03 mm), which encapsulated the core layer completely.

Uncapped or noncoextruded $HDPE_{0.4}$ /wood-flour composites (control) were also produced using coextrusion die to investigate the effect of a cap layer on the weathering of the WPCs. Manufacturing of the control samples included the twin screw extruder with a coextrusion die using the processing conditions similar to those mentioned above for core layers.

2.3. Accelerated weathering tests

An accelerated UV radiation weathering chamber simulates damaging effects of long term outdoor exposure by exposing test samples to ultraviolet radiation, moisture and heat. The QUV weatherometer from Q-Lab Corporation housed both coextruded and noncoextruded control samples. Tests carried out according to the procedure outlined the ASTM G 154 included a 12 h cycle consisting of 8h UVA-340 radiation at 60 °C, 15 min water spray, and 3 h 45 min condensation at 50 °C.

2.4. Scanning electron microscopy

Scanning electron microscopy pictures taken using JEOL JSM-6400 SEM at 12 kv accelerating voltage assisted monitoring the formation of cracks on the surface layer of control and cap layer of coextruded composites exposed to UV light. Moisture removal consisted of oven-drying the weathered samples at 105 °C followed by gold coating prior to observation.

2.5. UV-vis reflectance spectroscopy

A Lambda 25 UV-vis spectrophotometer (Perkin Elmer) functioned as the means in acquiring measurements of the UV-vis diffuse reflectance spectra of the HDPE $_{1.2}$ (for cap layer) and the HDPE $_{0.4}$ (used polymer matrix in both core layer of coextruded composites and uncapped WPCs). The scans were run from 600 to 250 nm with data interval of 1 nm. The scanning speed was set at 240 nm/min.

2.6. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) analysis was carried out on a Physical Electronics Phi 5400 ESCA System, (Physical Electronics USA, Chanhassen, MN) using a non-monochromatic Mg source and a takeoff angle of 45° relative to the detector. A low resolution scan from 0 to 1100 eV binding energy was used to determine the concentration of each element present on the surface of the samples, along with the oxygen to carbon (O/C) atomic ratio, whereas a high resolution scan of the C_{1s} region from 280 to 300 eV with a take-off angle of 45° C was performed to further analyze the chemical bonding of the carbon atoms. The binding energy scale was shifted to place the main hydrocarbon C_{1s} feature present at 285.0 eV. The degree of surface oxidation was calculated by the ratios of oxidized-to-unoxidized carbon atoms (C_{1s} peaks) using the following equation developed in our previous study [1-3]:

$$C_{\text{ox/unox}} = \frac{C_{\text{oxidized}}}{C_{\text{unoxidized}}} = \frac{C2 + C3 + C4}{C1}$$
 (1)

Carbon component C1 arises from carbon atoms bonded only to carbon and hydrogen atoms (C-C/C-H), C2 from carbon atoms bonded to a single oxygen atom, other than a carbonyl oxygen (C-OH), C3 from carbon atoms bonded to two noncarbonyl oxygen atoms or to a single carbonyl oxygen atom (O-C-O, C=O), and C4 from carbon atoms, which are linked to a carbonyl and a noncarbonyl group (O-C=O) [1].

2.7. Color measurements

The procedure outlined in ASTM D2244 served as the means by which to determine the color measurements on the surfaces of coextruded and control samples. A Minolta CR-420 Chroma Meter (Minolta Corp., Ramsey, NJ) measured the color in L*a*b* coordinates at three locations on each sample using the Commission Internationale d'Eclairage (CIELAB 1976 color space) three-dimension color space system. In this system, L* axis (+L* for light, -L* for dark) represents the lightness, a* (+a* is for red, -a* for green), and b* (+b* for yellow, and -b* for blue) the chromaticity coordinates. At least four replicates were measured for each formulation to obtain the average values of color. Calculations incorporated the values of lightness and chromaticity coordinates before and after weathering tests to determine the discoloration (Δ E*) of the weathered samples using the following equation:

$$\Delta E = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}}$$
 (2)

with ΔL^* , Δa^* , and Δb^* as the difference of initial and final values of L^* , a^* , and b^* .

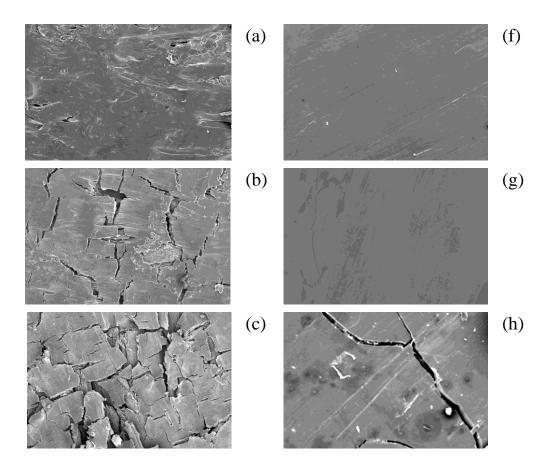
3. Results and discussion

3.1. Morphology and surface characteristics of weathered composites

Investigations have shown that wood flour filled HDPE composites manufactured by different processes (injection and extrusion) undergo morphological and chemical changes in

surface characteristics as they weather due to the accelerated cyclic UV/water spray actions [3,7]. Using SEM, FTIR, and XPS techniques, Stark and Matuana demonstrated that exposure to cyclic UV actions causes surface cracking of the matrix and degradation of the lignin portion of the wood particles. Whereas exposure to water spray causes wood particles to swell, which not only creates microcracks in the matrix, but also wash away loose wood particles, loose cellulose, and degraded lignin at the wood surface [3]. Similar techniques are used in this study to understand the effect of coextruding a cap layer onto WPC surface on the photodegradation of the composites. Fig. 1 shows the micrographs of the surfaces of both uncapped (control) and coextruded composites before and after weathering.

Prior exposure to UV/water spray cycling, coextruded WPC surface [Fig. 1(f)] was relatively smoother than the surface of uncapped WPC [Fig. 1(a)] mainly due to the presence of a thin HDPE layer on the surface of coextruded composites. Improper encapsulation of wood particles by the matrix could also account for the rougher surface of uncapped WPC. As a result, cracks appeared faster (after only 192 h) and more degradation occurred on the surface of uncapped WPC upon accelerated weathering [Fig. 1(b) to (e)] than the coextruded composite surface [Fig. 1(g) to (j)], owing to the swelling and shrinking of wood particles after absorbing and desorbing moisture during weathering water spray cycle [3]. In contrast, surface cracking did not appear on the surface of coextruded composites until 432 h of accelerated weathering [Fig. 1(h) to (j)]. The presence of an HDPE-rich layer on coextruded WPC surface retarded the formation of cracks in composites by delaying water sorption during weathering.



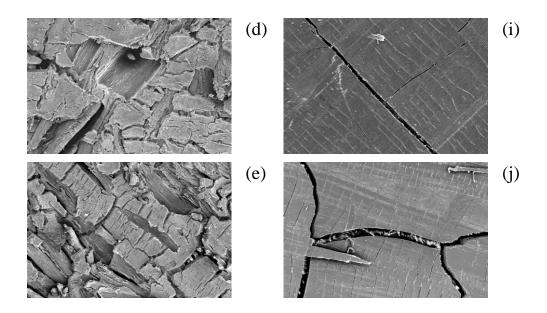


Figure 1. SEM (×80k) of surface of noncoextruded WPCs (left column) and coextruded WPCs (right column) as a function of UV radiation exposure times: (a and f) 0 h, (b and g) 432 h, (c and h) 744 h, (d and i) 1392 h, and (e and j) 1952 h).

These results also imply that the transparent cap layer onto WPC did not block all the UV radiations of UVA-340 lamps so that some ultraviolet light reached the surface of the inner layer of coextruded composites (i.e., the surface of WPC underneath the cap weathering layer) during experiments. Moreover, the UV-vis spectra of the polymers used for cap (HDPE_{1,2}) and core (HDPE_{0,4}) illustrated in Fig. 2 clearly indicate that almost 85% of visible light could penetrate the HDPE_{1,2} used as outer layer in coextruded composites. The film absorbed only around 15-25% light in the UVA-340 radiation region (295-365 nm).

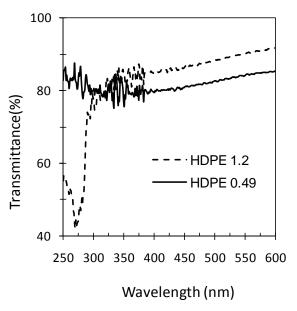


Figure 2. UV transmission spectra of films $HDPE_{1,2}$ (cap layer) and $HDPE_{0,4}$ (core).

Results obtained from XPS spectroscopy analysis provide evidence of lignin decay and formation of oxygenated products on composite surfaces. Table 1 summarizes the atomic concentrations of oxidized carbons, i.e., carbon atoms connected to oxygen atoms (C2, C3, and C4) and unoxidized carbon (Cl) obtained from the assignment and ratios of various peak components calculated from the decomposed C_{1s} peak. The C1 atomic ratio decreased after weathering, indicating lignin decay on the surface of composites, which was accompanied by a significant increase in the concentration of oxidized carbon atoms (C2 + C3 + C4) or the degree of surface oxidation (C_{ox}/C_{unox}). These results suggest the presence of surface rich in oxygenated products such as functional carbonyl groups of wood particles. The degree of surface oxidation showed two distinct trends. For uncapped composites, it increased with exposure time, reaching a maximum value at 192 h, after which it decreased. This was expected because of wood components were washed away during weathering. In contrast, the degree of surface oxidation steadily increased in coextruded because the cap layer prevented removal of loose wood components on the surface of the samples.

Table 1. C_{1s} peak analysis at HDPE, wood fiber, and WPCs surface and at coextruded WPCs interface determined by high-resolution XPS scan.

Carbon types	Exposure times (h)							
- -	0	192	432	744	1392	1952		
Uncapped WPC (control)								
C1	93.1	70.7	80.0	75.4	81.8	78.7		
C2	4.5	15.8	12.8	13.4	11.0	15.3		
C3	2.4	7.8	4.1	7.2	3.8	4.6		
C4	0	5.7	3.2	4.0	3.5	1.4		
C_{ox}/C_{unox}	0.07	0.41	0.25	0.33	0.22	0.27		
Coextruded composites						·		
C1	90.5	87.1	86.9	86.6	83.8	82.4		
C2	7.2	10.2	10.9	10.0	11.4	12.6		
C3	2.3	2.0	2.1	2.8	3.4	3.4		
C4	0	0.7	0.1	0.6	1.4	1.7		
C_{ox}/C_{unox}	0.10	0.15	0.15	0.15	0.19	0.21		

3.2. Color analysis

Fig. 3 illustrates the visual appearance of uncapped and coextruded composites before and after weathering and Table 2 summarizes the color parameters measured on these samples. Before weathering, the presence of cap layer did not affect the color of coextruded composites since both uncapped WPCs (control) and coextruded samples had similar visual appearance (Fig. 3). The lightness (L*), red-green (a*) and yellow-blue (b*) color coordinates of unexposed samples confirm this observation since both uncapped and coextruded composites had similar lightness and chromaticity values (Table 2). The transparency of the thin HDPE_{1.2} film coextruded onto the composites could account for the appearance similarities between the uncapped and coextruded composites before exposure to UV radiation. However, exposure to UV radiation resulted in two distinct trends in the visual appearances of the samples (Fig. 3). The surface of uncapped WPC

(control) lightened continuously upon UV radiation, as indicated by a constant increase in L* value and significant loss in both redness (a*) and yellowness (b*) (Fig. 3 and Table 2). Conversely, the discoloration of coextruded composites occurred in two different stages. They first darkened up to approximately 744 h of UV exposure and then experienced lightening as the exposure time increased (Fig. 3). The values of lightness, redness, and yellowness listed in Table 2 confirm this opposite trend. Darkness and yellowness observed in this stage of degradation of coextruded composites could be attributed to quinone chromophoric structures generated by the photodegradation of lignin whereas redness is controlled by the extractive contents in wood [9,19,20].

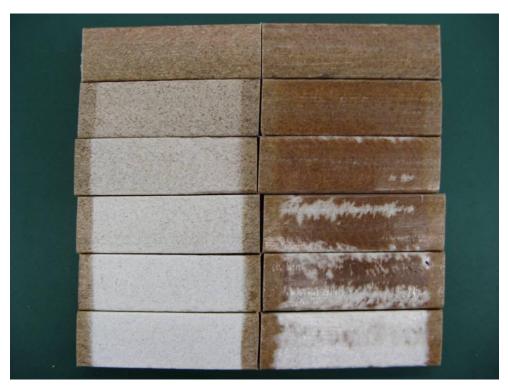


Figure 3. Visual appearance of uncapped WPCs (left column) and coextruded WPCs (right column) as a function of weathering exposure times (0, 192, 432, 744, 1392, 1952 h).

Overall, the surface of uncapped composites (control) experienced a quick lightening with a loss of yellowness and redness and underwent more discoloration (ΔE) than coextruded counterparts (Table 2) due to the photodegradation of wood components (Fig. 3). Uncapped composites experienced quicker lightening because water spray and condensation facilitated the removal of degraded wood component and formation of cracks, thus accelerating fading. The loss of degraded wood components on the surface of weathered composites could not be prevented due to poor adhesion between the filler and matrix [3].

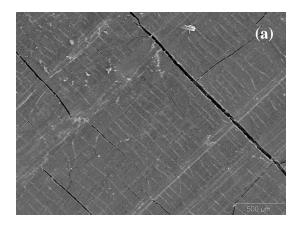
Table 2. Color parameters of control and coextruded samples before and after weathering.

Color parameters	Exposure times (h)							
	0	192	432	744	1392	1952		
Uncapped WPC (control)								
L*	59.4	70.8	81.3	83.2	84.9	88.1		
a*	7.0	4.7	2.8	2.1	0.9	1.1		
b*	18.2	13.1	9.3	6.5	3.4	3.9		
$\Delta \mathrm{E}$	-	12.6	24.0	27.0	30.1	32.3		
Coextruded composites								
L*	55.7	50.6	50.4	49.2	51.8	62.9		
a*	7.2	10.0	10.5	10.9	9.8	2.0		
b*	17.8	20.5	19.2	17.9	13.3	5.6		
$\Delta \mathrm{E}$	-	6.2	6.4	7.5	6.4	15.1		

However, for coextruded composites, the cap layer prevented both the removal of both degraded wood components and wood flour from the surface of weathered samples. Consequently, color change of coextruded composites was mainly dependent on photochemistry reactions occurring at the interface, which resulted in darkening other than lightening. Moreover, the darkening of coextruded WPCs clarified the mechanism of fading observed in uncapped wood plastic composites (control). Photooxidation of wood components itself would not lead to the fading of uncapped composites since fading occurs primarily due to the loss of colored components at the surface as well as the increase in roughness [19,21].

Conversely, the surface of coextruded composites initially darkened and then lightened with the failure of the cap layer. Darkening is due to the degradation of WPCs at the interface underneath the HDPE_{1.2} cap layer since the hydrophobic HDPE cap layer prevented removal of degraded wood components by water spray. However, the cap layer experienced a quicker failure after 744 h weathering. Since water spray eroded the surface, tensile and compressive stresses would be induced to the cap layer due to the variation of temperature and relative humidity occurring during the wet weathering cycle test [22]. Stresses damaged the cap layer integrity and accelerated the photodegradation, resulting in the formation of cracks at the cap layer and delamination between the cap layer and the core layer (Fig. 1). Moreover, after water entered the interface through cracks, it washed away the water-soluble degraded wood component, thus causing the fading of composites underneath the cap layer of coextruded samples.

Fig. 4 shows the micrographs of HDPE cap layer in the "white" area and "brown" area at the surface of coextruded samples weathered for 1392 h. Large and deep cracks were present in "white" area [Fig. 4(a)], implying that water could reach the interface through these cracks and wash away degraded wood components. It is believed that cracks at the surface of the HDPE cap layer caused light diffusion, resulting in a whitening effect. Therefore, both the cap layer and the interface made contributions to fading in the "white" area. By contrast, only small and narrow surface cracks were present in the "brown" area [Fig. 4(b)], which made it difficult for water to penetrate the interface through these areas. Thus the color in these areas appeared brown instead of white because most of chromophoric compounds generated by photodegradation of lignin were not removed from the interface between the core and cap layers.



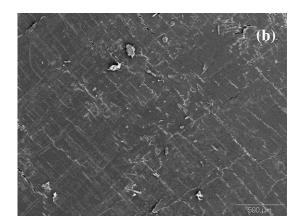


Figure 4. Micrograph of HDPE cap layer in "white" area (a) and "brown" area (b) at the surface of weathered coextruded samples.

3.3. Discoloration mechanisms of WPCs

The results of this study indicate that the discoloration mechanisms of WPCs depend on the degree of the encapsulation of the fiber by matrix and are related to whether the degraded wood components remain or not on the surface of WPCs upon UV weathering.

For uncapped WPCs, photooxidation of wood components combined with the loss of degraded wood components due to water spray constitute the main factors for fading, i.e., continuous lightening of WPCs during weathering. The increased roughness of surface due to the degradation of polymer matrix could also account for the continuous fading of uncapped WPCs.

Coextruded composites darken first because the hydrophobic cap layer over WPCs prevents water/moisture to penetrate the wood-plastic composites underneath the outer layer to wash away water soluble extractives from wood and/or other chromophoric compounds generated by photodegradation of lignin. This action reduces the negative effect of water on weathering. In contrast, as the exposure time increases, the cap layer cracks, water penetrates the interface washing away water soluble extractives from wood, leading to the lightening of the interface.

These results suggest that the discoloration of WPCs upon UV weathering is a combination of both chemical and physical changes. Chemical changes are induced by the photooxidation of wood components, which determines the initial color change. The composites become dark and yellow if the adhesion between fibers and matrix is strong to prevent surface erosion and removal of degraded wood components. Otherwise, the loss of degraded wood components could occur, and if combined with the degradation of polymer matrix which increases the roughness of WPC surface, leading to in fading of the WPC surface. Therefore, whether the degraded wood components remain on the surface of WPCs or not would determine the direction of the long-term color change of WPCs upon UV weathering.

4. Conclusions

Both noncoextruded and coextruded WPCs with a clear HDPE cap layer were exposed to accelerated weathering cycles including UV radiation, water spray, and condensation. The color, functional groups, and degree of oxidation of samples before and after weathering were analyzed by

chroma meter, XPS, and UV vis. The following conclusions can be drawn from the experimental results:

The color of noncoextruded and coextruded WPCs upon weathering changed in different directions, revealing the discoloration mechanism of WPCs.

Overall, the surface of uncapped composites (control) experienced a quick lightening with a loss of yellowness and redness and underwent more discoloration (ΔE) than coextruded counterparts due to the photodegradation of wood components. Uncapped composites experienced quicker lightening because water spray and condensation facilitated the removal of degraded wood components and formation of cracks, thus accelerating fading. The loss of degraded wood components on the surface of weathered composites could not be prevented due to poor adhesion between the filler and matrix. This mechanism indicates the critical role of wood fiber-polymer matrix interface adhesion on the discoloration of WPCs.

Conversely, the surface of coextruded composites initially darkened and then lightened with the failure of the cap layer. Darkening is due to the degradation of WPCs at the interface underneath the HDPE cap layer since the hydrophobic HDPE cap layer prevented removal of degraded wood components by water spray. However, the cap layer experienced a quicker failure after 744 h weathering. Since water spray eroded the surface, tensile and compressive stresses would be induced to the cap layer due to the variation of temperature and relative humidity occurring during the wet weathering cycle test. Stresses damaged the cap layer integrity and accelerated the photodegradation, resulting in the formation of cracks at the cap layer and delamination between the cap layer and the core layer. Moreover, after water entered the interface through cracks, it washed away the water-soluble degraded wood component, thus causing the fading of composites underneath the cap layer of coextruded samples.

Overall, the hydrophobic cap also prevented wood fiber access to moisture/water, reducing the negative effect of water on weathering. Moreover, the cap layer absorbed some UV light and reduced the availability of oxygen at the interface of coextruded composites, thus decreasing the photodegradation rate. The oxidation rate at the interface of coextruded WPCs was demonstrated by XPS spectra.

Acknowledgements

The authors gratefully acknowledge the USDA-CSREES Grant-Advanced Technology Applications to Eastern Hardwood Utilization (Grant No. 2008-34158-19510) for the financial support for this research work.

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