Polymer Degradation and Stability 96 (2011) 97–106

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Ultraviolet weathering of HDPE/wood-flour composites coextruded with a clear HDPE cap layer

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ARTICLE INFO

Article history:
Received 6 July 2010
Received in revised form
7 October 2010
Accepted 23 October 2010
Available online 2 November 2010

Keywords:
Wood–plastic composites (WPCs)
Ultraviolet radiation
Weathering
Discoloration mechanism
Coextrusion
FTIR and XPS

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, FTIR-ATR, XPS, SEM, and UV vis measurements accounted for the analysis of discoloration, functional groups, 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.

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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. The presence of the hydrophobic polymer phase in WPCs improves the durability in terms of resistance to water absorption and biological decay compared to that of solid wood [1–4]. However, 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 [5–14]. A significant feature of WPCs, aesthetic value, becomes compromised through discoloration, making it a major concern.

Controlling the discoloration of WPCs upon weathering requires a comprehensive understanding of weathering mechanisms. Photodegradation of WPCs, also understood as the weathering of the major components of WPCs (wood and polymer), results from the combined effects of light, water, oxygen, and heat.

All main polymeric components of wood, such as cellulose, hemicellulose, lignin, and extractives, suffer from photodegradation [15]. Because visible light (400–700 nm) carries energy less than 292.9 kJ/mol, it cannot provide sufficient energy to break the major chemical bonds in the wood components [15]. Thus, the photodegradation of wood results primarily from the ultraviolet aspect of sunlight. The degrees of photodegradation of wood components largely depend on their ability to absorb UV light. Because the location of most wood chromophores is in lignin, lignin accounts for 80-95% of light absorption of wood, making its photodegradation a significant contribution to wood discoloration [16]. Absorption of UV light initiates the photochemical reactions of wood surfaces leading to the formation of aromatic and other free radicals, which causes the degradation of lignin and photo-oxidation of cellulose and hemicelluloses, effectually causing discoloration [15,17]. Generally, wood in outdoor environments initially becomes yellow and brown due to the photooxidation of lignin, and then gray due to leaching of the degraded product of lignin [15]. This discoloration and yellowing of wood surfaces result from the loss of methoxyl content of lignin,

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doi:10.1016/j.polymdegradstab.2010.10.003

photo-dissociation of carbon-carbon bonds and formation of carbonyl-based chromophoric groups. Numerous studies report that wood exposed to artificial weathering (only exposure to UV radiation) darkens as the radiation time increases [15–18].

Similar to the photodegradation of wood, the photodegradation of polyolefins is a radical-based oxidative process. The presence of catalyst residues, hydroperoxide groups, and carbonyl groups introduced during polymer manufacturing, processing, and storage accounts for this similarity [19]. All of these species absorb UV light above 290 nm and initiate photochemical reactions. Photodegradation causes changes in all scales of polymer dimension, including the monomer unit (oxidation), the chain (crosslinking or chain scission), the morphology (breakdown of tie molecules and crystal), and on the macroscopic scale [20]. Diffusion of oxygen in the polymer controls polyolefin photodegradation. Density gradients due to oxidation gradients cause the stresses, which combined with chain scission, could initiate and propagate cracks. Cracks on the surface result in light diffusion (a whitening effect in appearance) and also lead to the mechanical properties loss [21].

Photodegradation of WPCs involves several factors including the wood flour content, coupling agents, manufacturing methods, and weathering conditions, among others. Matuana and Kamdem investigated the influence of accelerated artificial weathering on the color changes and tensile properties of PVC/wood-flour composites with various wood flour contents [6]. While the composites retained original tensile properties, they experienced severe discoloration (darkening) after weathering for 2600 h. PVC/wood-flour composites containing 15 phr wood flour darken more than those containing 30 phr and 45 phr wood flour. Conversely, reports indicate the opposite trend for weathered HDPE/wood-flour composites; the composites containing 50% wood flour lighten more than the counterparts with 25% wood flour [22]. Ndiaye and coworkers studied the effects of wood flour content and compatibilizer on the durability of HDPE-based and PP-based WPCs [23]. Their results indicated that the oxidation rate of the composites increases with wood content and decreases with the presence of compatibilizer due to better dispersion of wood flour in polymer matrix [23].

Examining the effect of weathering conditions (UV radiation with or without water spray) and manufacture methods (injection molding and extrusion) on the changes in lightness and flexural properties of HDPE/wood-flour composites, Stark and Matuana reported that the composites experienced more lightening and flexural properties loss when exposed to UV radiation with water spray cycle compared to UV radiation cycle alone [11–13]. Wood particle bleaching due to UV radiation and removal of water-soluble extractives by water spray caused the color fading of these composites. Not only did water spray accelerate oxidation reactions and facilitate light penetration into the composites, but it also removed water-soluble wood extractives, thus causing faster fading. Weathered injection-molded composites lightened more slowly than extruded ones due to the hydrophobic HDPE-rich surface layer that formed on the surface of injection molded composites [11–13].

Recent investigations studied the effects of natural and accelerated artificial weathering on the appearance and chemical changes of HDPE-based and PP-based WPCs [6–14,24]. The lightness, total color change, and wood loss increased with exposure time. PP-based WPCs experienced quicker photodegradation in terms of lightness and wood loss. Delignification and oxidation accounted for the increased lightness of weathered composites. Muasher and Sain also investigated the discoloration of HDPE-based WPCs exposed to natural weathering and reported that WPCs underwent two competing redox reactions upon UV exposure: the formation of paraquinone chromophoric structures generated by the oxidation of lignin, resulting in yellowing, as well as the reduction of the paraquinone structures to hydroquinones, leading to photobleaching [24]. The yellowing mechanism dominant during the first 250 hours of exposure preceded the photobleaching mechanism that became dominant with increased exposure time.

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 [7,22,24,25]. For example, adding photostabilizers and pigments provides protection against discoloration caused by UV radiation. Stark and Matuana studied the effects of an ultraviolet light absorber (UVA), a colorant, and two hindered amine light stabilizers (HALS, low molecular weight diester and secondary amine triazine) on the photostabilization of HDPE-based WPCs composites using a factorial design [25]. Because UVA absorbs some UV radiation and the colorant's ability to block the penetration of UV radiation, as well as masking the bleaching of wood fiber, UVA and colorant significantly lowered the lightness upon weathering. Conversely, the two HALS did not show significant effects on lightness. Investigation of five HALS (low, medium, and high molecular weight diester, and tertiary and secondary amine triazine) and combinations of HALS and UVA on the color changes of HDPE-based WPCs indicated that the molecular weight of diester HALS played an important role in the color changes [24]. Low molecular weight diester HALS shows high effectiveness in the initial stage due to their fast diffusion to the surface but alternatively, low effectiveness with increased exposure time due to their loss by surface evaporation [24]. Assuming the loss of color-imparting extractives from wood flour as responsible for fading, examinations studied the role of fiber pretreatment on the color stability of HDPE/wood-flour composites. As a result, fiber pretreatment methods included removing water-soluble extractives from wood flour and coloring wood flour with a water-based dye or an oil-based stain [22]. Whereas the removal of water-soluble extractives from wood flour and coloring wood flour with a water-based dye did not improve the color stability of the composites upon weathering, coloring wood flour with an oil-based stain significantly improved the color stability [22].

Although adding stabilizer or pigment into the entire composites improves their resistance to photodegradation, weathering primarily occurs at the surface of a material [6–15]. Pursuing a cost-effective means to cope with weathering would not favor adding photo stabilizers into the bulk of a material instead of the surface. The best approach in improving durability would involve adding photo stabilizers protection only on the surface of composite samples.

Several methods can provide a durable surface to withstand weathering. Coating, one of the methods widely used in the wood industry, provides protection against environmental damage such as weathering, biodegradation, and mechanical abrasion. For protection against photodegradation, opaque pigmented coatings block the UV/visible light but cover the aesthetics of wood. Conversely, semi-transparent and clear coatings maintain the natural appearance of wood, but the UV/visible light transparency of the coating results in the photodegradation of wood substrate and the resultant failure of the coating adhesion due to the photodegraded substrate [26–29].

Investigation of the photo-discoloration of UV-curable acrylic coatings and the underlying wood revealed that coating wood specimens with non-photostabilized UV-curable acrylic clear films such as aromatic urethane, aliphatic urethane, epoxy and silicone, fails to protect wood underneath the films against discoloration [27]. Both the coating films and wood specimens underneath these films experienced severe discoloration after exposure to UVA lamps at 60 °C for 12 h. Photodegradation of the interfacial layer led to flaking and peeling of the coating. Poor UV light resistance of the

clear films could account for the lower color stability of these coatings, as it reduces the intensity of UV light reaching the interface layer between wood surface and the films [27].

In a subsequent study, investigations examined the effect of photostabilized aliphatic or aromatic urethane-modified acrylic clear coatings on the photo-discoloration of coated wood as a means to reduce the intensity of UV light reaching the interfacial layer without changing the natural color of coatings and wood [29]. The evident screening effect of ultraviolet light absorbers (UVA) such as benzophenone and hydroxyphenyl benzotriazole resulted since their incorporation into coating films inhibited the photo-discoloration of wood coated with both aliphatic and aromatic urethane-modified acrylics (19–24 h exposure). The addition of HALS failed to reduce the discoloration of wood coated with aromatic urethane-modified acrylate containing UVA, attributable to its inability to capture the radicals produced by the photo-discoloration of aromatic urethane films. In contrast, observations focused on a synergetic effect of HALS for wood coated with aliphatic urethane-modified acrylic containing light absorbers. The addition of HALS further reduced the color changes of coated wood due to its actions in scavenging the free radicals produced from the photodegradation process and protecting light absorbers against the attack of free radicals [29]. However, difficulty arises in coating the plastic composite at the surface of WPCs due to the low surface energy of plastic. Coating also involves solvent evaporation, which often causes environmental concerns. Furthermore, the drying stage of coating requires additional time, reducing the efficiency of the assembly line.

Another method for providing a protective surface includes lamination. Melt fusion or an adhesive layer allow for the lamination of a surface layer over substrate. Nevertheless, delamination often occurs with the bending of the laminated composites [30]. Moreover, difficulty arises in the usage of lamination technology to manufacture a fully encapsulated structure in wood plastic composites rather than a planar layered structure.

Coextrusion, another method for providing a protective surface, can produce a multilayered product with different properties at outer and inner layers, thus offering different properties between surface and bulk [31,32]. 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 [33–37]. Because of water's significance in weathering of WPCs [11–13], 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 [37].

Therefore, 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, FTIR, 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/cm^3. Another HDPE (FORTIFLEX™ 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/cm^3. 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 min. 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.

The coextrusion system consisted of a coextrusion die connecting a twin screw extruder for the core layer and a single screw extruder for the cap layer, as described in detail in previous studies [33–37].

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 ± 0.03 mm), which encapsulated the core layer completely (Fig. 1).

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

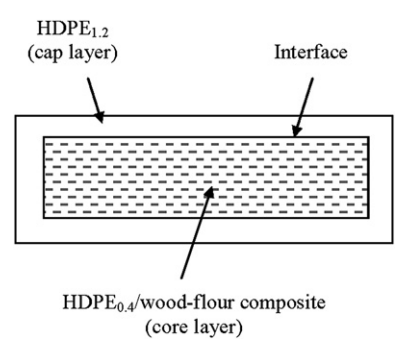

Fig. 1. Schematic of the cross section of coextruded HDPE/wood-flour composite.

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 8 h UVA-340 radiation at 60 °C, 15 min water spray, and 3 h 45 min condensation at 50 °C. The UVA-340 lamps give an excellent simulation of sunlight in the critical short wavelength region from 365 nm down to 295 nm. UVA-340 radiation, water spray, and condensation could simulate sunlight, rain, and dew, respectively. Water spray also could introduce thermal shock and mechanical erosion.

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. Fourier transform infrared spectroscopy

Perkin Elmer Spectrum 100 with attenuated total reflectance (ATR) acquired the Fourier transform infrared spectroscopy (FTIR) spectra. The surface of samples in contact with a ZnSe crystal had a 45° angle of incidence. Scans ran at a resolution of 4 cm^{-1} from 4000 to 650 cm^{-1}. Quantifying data used the net peak absorbance obtained after the baseline correction. Following the approach described by Stark and Matuana, the peak intensities of absorption bands at 1030, 1715, and 2915 cm^{-1} were used to calculate both wood and carbonyl indices using the following equations [8–10]:

$$\text{Wood index} = \frac{I_{1030}}{I_{2915}} \times 100 \tag{1}$$

$$\text{Carbonyl index} = \frac{I_{1715}}{I_{2915}} \times 100 \tag{2}$$

2.7. 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 [6–8]:

$$C_{\text{ox/unox}} = \frac{C_{\text{oxidized}}}{C_{\text{unoxidized}}} = \frac{C2 + C3 + C4}{C1} \tag{3}$$

with 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 non-carbonyl group (O–C=O) [6].

2.8. 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 (ΔE^*) of the weathered samples using the following equation [6]:

$$\Delta E = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \tag{4}$$

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 [8,11]. 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 [8]. 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. 2 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. 2(f)] was relatively smoother than the surface of uncapped WPC [Fig. 2(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

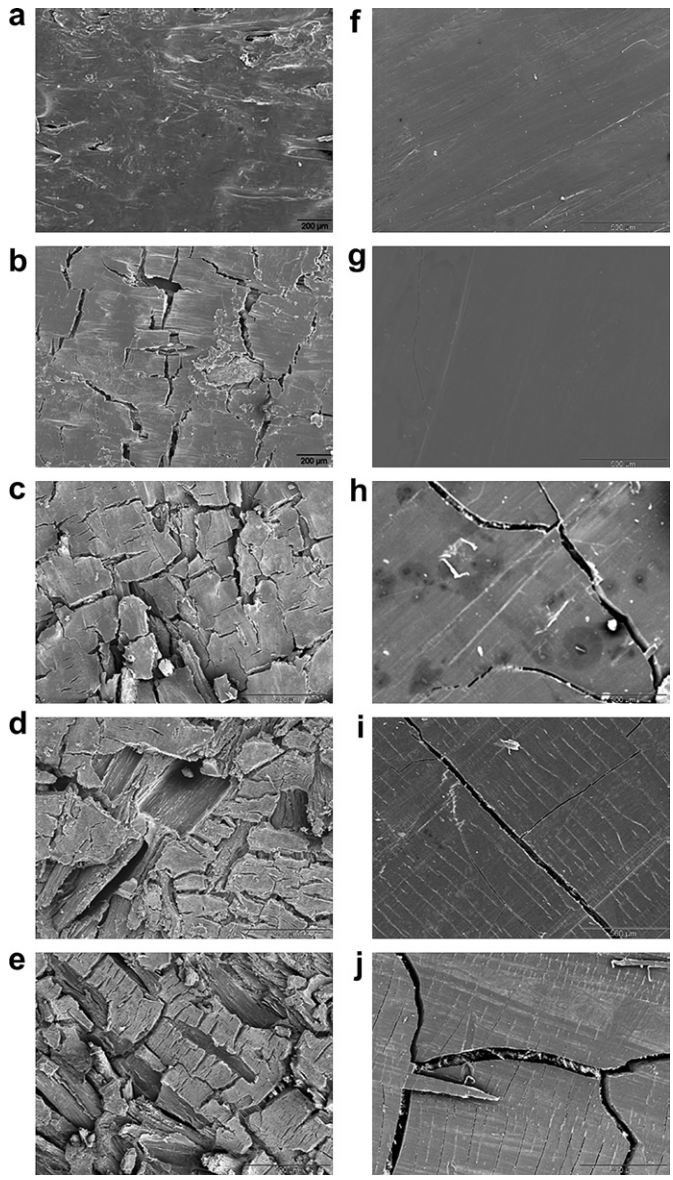

Fig. 2. SEM (×80 k) of surface of noncoextruded WPCs (left column) and coextruded WPCs (right column) as a function of UV radiation exposure times: (a and f) 0 h, (b and g) 432 h, (c and h) 744 h, (d and i) 1392 h, and (e and j) 1952 h).

surface of uncapped WPC upon accelerated weathering [Fig. 2(b)–(e)] than the coextruded composite surface [Fig. 2(g)–(j)], owing to the swelling and shrinking of wood particles after absorbing and desorbing moisture during weathering water spray cycle [8]. In contrast, surface cracking did not appear on the surface of coextruded composites until 432 h of accelerated weathering [Fig. 2 (h)–(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.

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 layer) during weathering experiments. Moreover, the UV–vis spectra of the polymers used for cap ($HDPE_{1.2}$) and core ($HDPE_{0.4}$) illustrated in Fig. 3 clearly indicate that almost 85% of visible light could penetrate the $HDPE_{1.2}$ used as outer layer in coextruded composites. The film

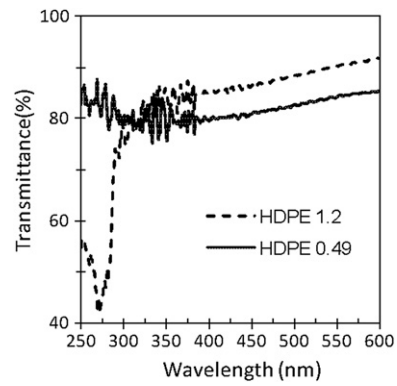

Fig 3. UV transmission spectra of films of $HDPE_{1.2}$ (for cap layer) and $HDPE_{0.4}$ (polymer matrix for uncapped WPC and core layer of coextruded WPCs).

absorbed only around 15–25% light in the UVA-340 radiation region (295–365 nm). Fourier transform infrared (FTIR) spectra of HDPE matrices before and after cyclic UV/water spray exposures corroborate this finding (Fig. 4). Distinct absorption peaks of HDPE are observed at around 2915, 2847, 1472, 1176, 730, and 718 cm^{-1} and Table 1 lists their wavenumbers along with the assignments of corresponding functional groups. The appearance of strong peak at 1713 cm^{-1} and 1176 cm^{-1} on the surface of HDPE [Fig. 4(b)] clearly indicates the evidence of photodegradation of the polymer used in both core and cap layers. Fig. 4(a) also shows important absorption bands in FTIR spectra associated with wood. Peaks associated with

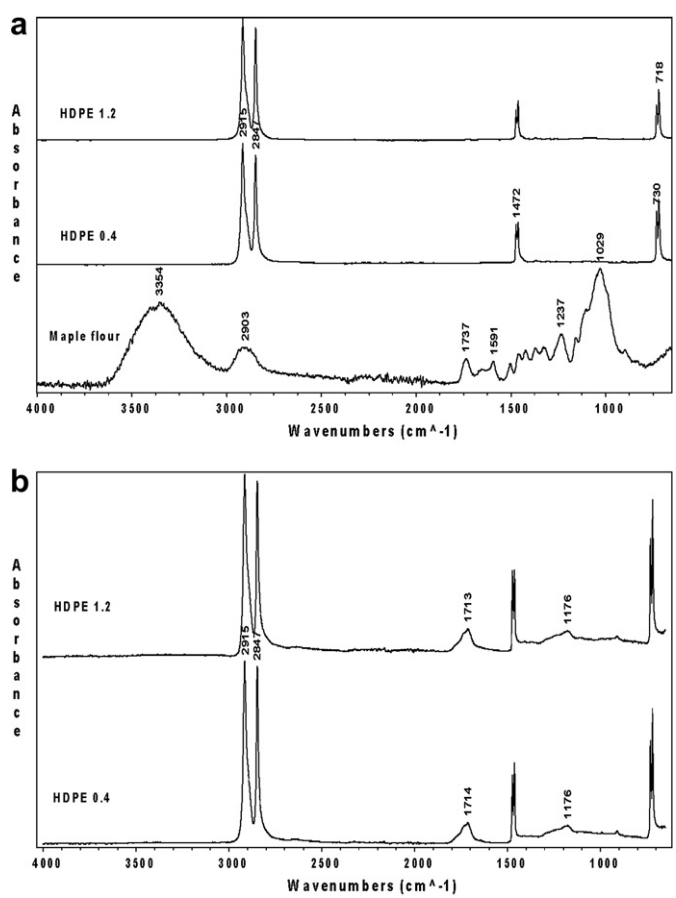

Fig. 4. FTIR spectra of wood flour (maple) and HDPE (a) before and (b) after exposure to 1952 h UV.

wood are clearly seen around 3354 (broad peak), 2903, 1737, 1591, and 1029 cm^{-1}.

The infrared spectra of uncapped and coextruded composites are illustrated in Figs. 5 and 6, respectively. Before exposure, both uncapped [spectrum (a) in Fig. 5] and coextruded [spectrum (a) in Fig. 6] composite surfaces combined the characteristics of wood particles and HDPE matrices (Fig. 4). However, evidence of photodegradation to the surface of composites was apparent in the spectra of UV-weathered samples [spectra (b) to (f) in Figs. 5 and 6]. The main spectral changes are seen at around 3300–3354 cm^{-1}, 1714–1738 cm^{-1}, and 1029–1033 cm^{-1} frequency ranges, which are characteristics to wood components [8,47–49].

Uncapped composite surface (Fig. 5) experienced a fast and severe wood component loss after exposure to accelerated UV/water spray weathering than the coextruded counterparts (Fig. 6). Unlike coextruded composite surface, a significant decrease in the intensity of peaks at 3300–3354 cm^{-1} (OH in cellulose) and 1029–1033 cm^{-1} (C–O in cellulose and primary alcohols of lignin) occurred on the surface uncapped composites even after only 192 h exposure and these peaks almost disappeared as the weathering exposure time increased. Wood index data listed in Table 2 support these findings. It is believed that water spray cycle during weathering washed away the loose wood components (lignin decay) and the presence of microcracks provided a channel for their fast removal on the surface of the uncapped composites.

Although there were cracks on the surface of coextruded composite as shown in Fig. 2, the presence of a thin HDPE cap layer prevented the complete loss of wood components by the water spray as indicated by the intensity peak at 1029–1033 cm^{-1} (Fig. 6) and percent wood index (Table 2). Two main reasons could account for the retention of the wood component at the surface of the coextruded composite: (i) the presence of HDPE cap layer reduced the oxygen available for oxidation at the interface between the inner and outer layers of coextruded composites and (ii) HDPE cap absorbed some UV energy (Fig. 3 shows that $HDPE_{1,2}$ absorbed 15–25% light in the UVA-340 irradiance region) to cause photodegradation.

Furthermore, composites experienced surface oxidation, irrespective of the cap layer. This can be clearly seen by the increased carbonyl index (Table 2) and area under the absorption bands in the region 1650–1750 cm^{-1}, assigned to carbonyl groups in carboxylic acid, acetyl ester, or quinine (Figs. 5 and 6). Photodegradation of lignin leads to the formation of these carbonyl groups and thus the increase in intensity of the carbonyl bands. Several authors have correlated the increased integrated area or peak height of this band and carbonyl index with the oxidative photodegradation of polymer [45,46], wood [15–17], and wood–plastic composites [9,10,14] due to the presence of oxygenated products.

The results obtained from XPS spectroscopy analysis provided supporting evidence of lignin decay and formation of oxygenated products on composite surfaces. Table 3 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 detected in FTIR spectra (Figs. 5 and 6). 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 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.

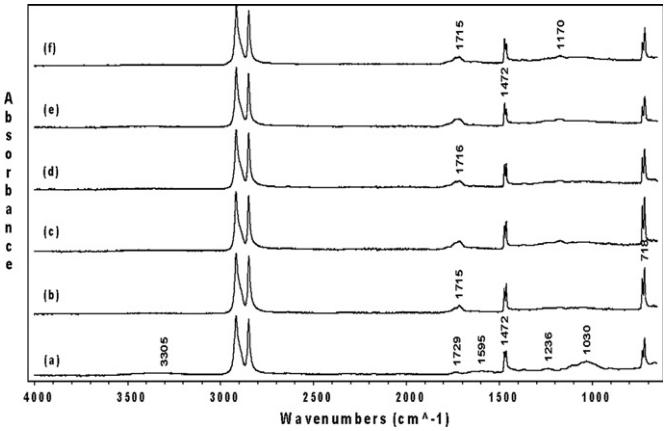

Fig. 5. FTIR of the surface of uncapped WPCs as a function of weathering time (a) unexposed or control, (b) 192 h, (c) 432 h, (d) 744 h, (e) 1392 h, and (f) 1952 h.

Table 1
Assignment of absorption bands of IR spectrum.

Wave numbers (cm^{-1})	Assignments [6–10,38–49]
Wood particles	
3354	–OH stretching in hydroxyl groups originating mainly from cellulose
2903	CH stretching in $-CH_2-$ groups
1729–1737	C=O stretching (ester carbonyl)
1714–1717	C=O stretching (acid carbonyl)
1591	Aromatic ring stretching (lignin)
1029	C–O stretch in cellulose and deformation in the primary alcohols of lignin
HDPE	
2915	CH_2 stretching of CH_2, CH_3 (asym.)
2847	CH_2 stretching (sym.)
1713	C=O stretching (aci carbonyl)
1472	CH_2 deformation (scissor vibration), crystalline
1462	CH_2 deformation (scissor vibration), amorphous
1176	C–O stretching (ester)
730	CH_2 rocking vibration, crystalline
718	CH_2 rocking vibration, amorphous

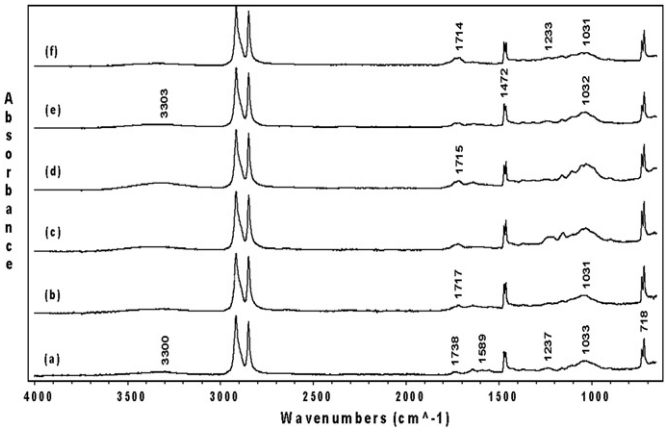

Fig. 6. FTIR of the interface of coextruded WPCs as a function of weathering time (a) unexposed or control, (b) 192 h, (c) 432 h, (d) 744 h, (e) 1392 h, and (f) 1952 h.

Table 2
Concentrations of oxidative products on uncapped and coextruded WPCs.

Exposure times (h)	Wood index (%)		Carbonyl index (%)	
	Uncapped WPCs	Coextruded WPCs	Uncapped WPCs	Coextruded WPCs
0	21	30.8	6.6	8.8
432	0	36.4	16.4	11.9
1392	0	37.3	19.7	15.8
1952	0	26.7	18.8	19.0

3.2. Color analysis

Fig. 7 illustrates the visual appearance of uncapped and coextruded composites before and after weathering and Table 4 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. 7). 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 4). 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. 7). 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. 7 and Table 4). 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. 7). The values of lightness, redness, and yellowness listed in Table 4 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 [15,50,51] whereas redness is controlled by the extractive contents in wood [50].

Color characteristics of solid wood (maple wood) and neat HDPE bars exposed to UV radiation and water condensation were measured to understand this opposite trend. Fig. 8 illustrates the discoloration as well as the changes in lightness, yellowness, and redness of these samples as a function of UV radiation time. While UV radiation had a small influence on the discoloration of HDPE films, it significantly impacted the surface of solid wood (Fig. 8), suggesting that wood components made major contribution to the color changes in both uncapped and coextruded composites. Since the cap layer ($HDPE_{1.2}$) did not fade too much and the ultraviolet light penetrates the transparent film (Fig. 3), discoloration of coextruded composites could have occurred at the interface between the wood plastic composites in the inner layer and the $HDPE_{1.2}$ in the outer layer.

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 4) due to the photodegradation of wood components (Fig. 8). 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 [8].

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

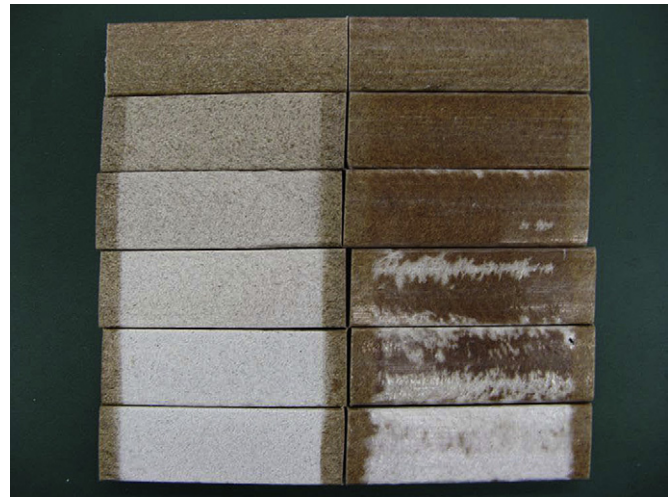

Fig. 7. Visual appearance of uncapped WPCs (left column) and coextruded WPCs (right column) as a function of weathering exposure times (0, 192, 432, 744, 1392, 1952 h).

Table 3
C_{1s} peak analysis at 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

Table 4
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
ΔE	–	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
ΔE	–	6.2	6.4	7.5	6.4	15.1

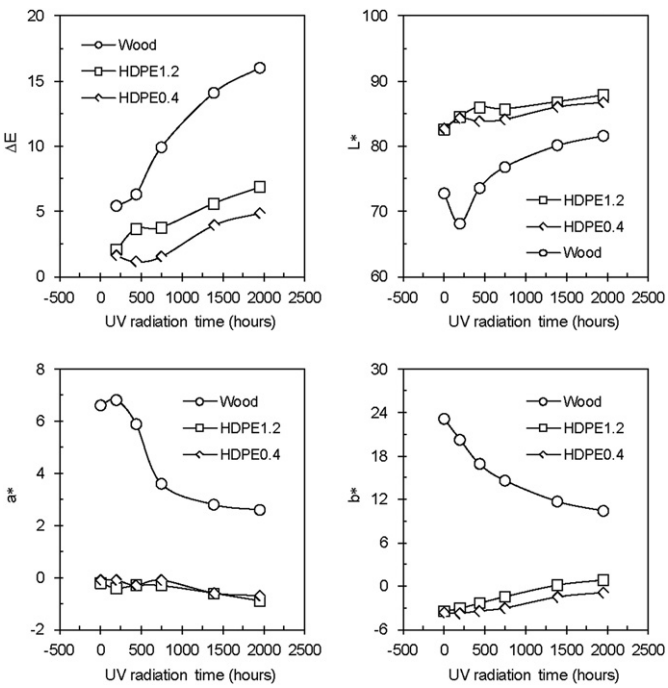

Fig. 8. Color parameters for solid wood (maple), HDPE0.4, and HDPE1.2.

components at the surface as well as the increase in roughness [50,52,53].

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 [54]. 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. 2). 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. 9 shows the micrographs of HDPE cap layer in the "white" area and "brown" area at the surface of coextruded samples weathered for 1392 h (Fig. 7). Large and deep cracks were present in "white" area [Fig. 9(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. 9(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.

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 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.

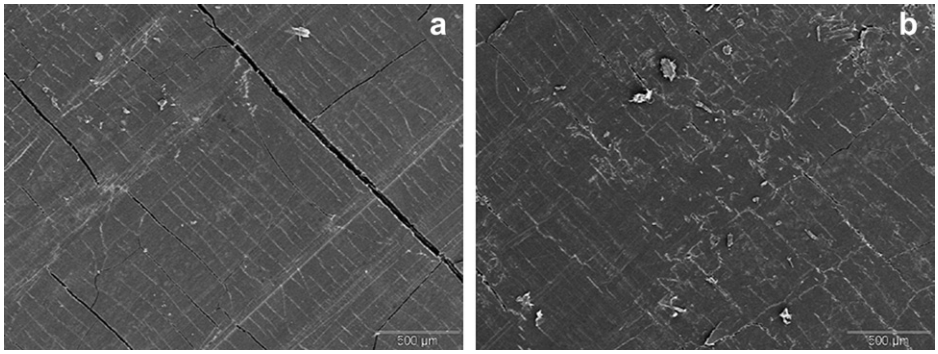

Fig. 9. Micrograph of HDPE cap layer in "white" area (a) and "brown" area (b) at the surface of weathered coextruded samples.

Based on these proposed mechanisms, several weathering-induced discoloration phenomena reported in literature could be explained. Investigations have shown that PVC-based WPCs darken after UV radiation [6] whereas polyolefin-based WPCs lighten [11–13,22]. Owing to PVC polarity, it is believed that the interfacial adhesion between wood fiber and polymer matrix is much better in PVC-based WPCs than that in polyolefin-based counterparts, making the removal of wood components more difficult on the surface of PVC-based WPCs during the weathering [6]. On the contrary, wood components are easily washed away on the surface of polyolefin-based WPCs upon UV radiation/water spray cycle, leading to fading. It appears that strong adhesion between wood fiber and polymer matrix would reduce the loss of wood components upon weathering. Consequently, the extent of wood fiber encapsulation by the polymer matrix is crucial for the discoloration of WPCs. Generally, lower the wood flour content, better the fiber encapsulation by the matrix, resulting in less fading for polyolefin-based WPCs [11–13,22] or more darkening for PVC-based WPCs [6].

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, FTIR-ATR, 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 decreased lignin degradation rate and the oxidation rate at the interface of coextruded WPCs were demonstrated by FTIR and XPS spectra, respectively.

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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