Influence of a Stabilized Cap Layer on the Photodegradation of Coextruded High Density Polyethylene/Wood-Flour Composites

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The effect of light stabilizer's addition method into wood-plastic composites (WPCs), i.e., surface versus bulk, on their photostability was evaluated. Blends of ultraviolet absorbers (benzotriazole or hydroxyphenyltriazine) with a hindered amine light stabilizer were used as the stabilizing additives. Both unstabilized and photostabilized uncapped (control) samples, as well as coextruded WPCs counterparts, were exposed to up to 3000 h of accelerated artificial weathering. The light transmittance, surface morphology, and color of the samples before and after weathering were analyzed by UV-vis spectroscopy, SEM, and Chroma Meter. The experimental results indicated that the method of adding the light stabilizer had a significant effect on the WPC photostability. While bulk addition reduced the degree of fading in uncapped composite, it did not suppress it completely. On the other hand, coextruded WPCs with photostabilized cap layers showed no visible signs of fading, thus clearly indicating that the stabilized cap layers blocked most of the UV radiation, and thereby prevent of UV light to reach the surface of the inner layer of coextruded composites. Cost-analysis considerations indicated that 50 times more light stabilizer was needed when it was incorporated into the bulk of the composites rather than in the cap layer of coextruded samples. Clearly, these results suggest that adding light stabilizers at the surface of WPCs not only protects them against UV degradation, but also is a most efficient and cost-effective method of photostabilization than bulk addition. J. VINYL ADDIT. TECHNOL., 19:239–249, 2013. © 2013 Society of Plastics Engineers

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INTRODUCTION

Wood-plastic composites (WPCs) have experienced significant market expansion in recent years as a replacement for solid wood, mainly in outdoor applications [1]. Originally marketed as weather-resistant products with little to no maintenance compared to solid wood, their performance expectations fail to accounting for the results of their exposure to outdoor environments with ultraviolet radiation and moisture, which prevent them from retaining their new appearance without maintenance [1].

Studies have shown that WPCs can absorb moisture in a humid environment because of the highly hydrophilic nature of the wood flour in the composites, especially at high loading levels, which makes the products more prone to microbial growth and biological decay, thus affecting their appearance [2–6]. Moisture absorption also reduces the adhesion between the filler and the polymer matrix, an effect which results in modest loss of mechanical properties [7]. Aware of these durability issues, the industry continues to take steps to ensure the long-term performance of these products. In particular, the WPC producers seeking improved products focus on water absorption resistance, color and appearance retention, and physico-mechanical property retention, as well as mould and mildew resistance over time [1–21].

Several proposed approaches substantially reduce or delay the moisture and water uptake of WPCs. Reports designate the use of performance enhancing additives such as lubricants, coupling agents, and other compatibilizers; encapsulation of exposed wood during compounding; or the use of a protective coating as methods to decrease the moisture uptake of WPCs [19]. Current approaches to improving their weathering resistance focus on the bulk of WPCs, that is, incorporation of additives

into the entire product or surface treatment of the wood fiber [11, 19–21]. Although adding light stabilizer into the entire composites improves their resistance to photodegradation, weathering occurs primarily at the surface of a material [4–6, 10–17]. Pursuing a cost-effective means to cope with weathering would not favor adding photostabilizers into the bulk of the material instead of on the surface. The best approach in improving durability would involve adding photostabilizers protection only on the surface of composite samples.

Investigations have recently demonstrated that covering the WPCs with hydrophobic layers decreases their moisture absorption. A cap layer of polyolefin or PVC coextruded over WPCs provided improved moisture resistance compared to that of the uncapped control WPCs [22–26]. Unfortunately, in a subsequent study, photodiscoloration of the cap layer and the underlying wood-plastic composite core revealed that coextruding a nonphotostabilized clear hydrophobic high-density polyethylene (HDPE) cap layer over WPCs failed to protect the WPC underneath the cap layer against discoloration [27]. Both the cap layer and the underlying core layer experienced severe discoloration after exposure to UVA lamps at 60°C for approximately 2000 h [27]. The surface of coextruded composites initially darkened and then lightened with the failure of the cap layer. Darkening was due to the degradation of the WPCs at the interface underneath the cap layer, since the hydrophobic cap layer prevented the removal of degraded wood components by water spray. However, the cap layer experienced a quicker failure after 744 h of weathering. Since water spray eroded the surface, it was believed that tensile and compressive stresses were induced to the cap layer because of the variations of temperature and relative humidity occurring during the wet-weathering cycle test. Stresses damaged the cap layer integrity and accelerated the photodegradation, thereby resulting in the formation of cracks in this layer and delamination between it and the core layer. Moreover, after water entered the interface through cracks, it washed away the water-soluble degraded wood components, thus causing the fading of the composites underneath the cap layer of coextruded samples [27].

Since UV light can transmit through the unprotected cap layer, both the cap layer and the interface underneath it experience photodegradation, thus suggesting the need for photostabilization of the composite. Consequently, this study evaluated the effect of photostabilization on the ultraviolet degradation of coextruded HDPE/(wood flour) composites. Particular emphasis was placed on assessing the effects of the methods of adding the light stabilizer composites [only at surface (or cap layer) versus into the entire WPCs (or bulk addition)] on the photostability of the composites. Both the product performance and the material cost were assessed in order to determine the most effective approach.

EXPERIMENTAL

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. The material for wood flour was 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, in order 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.

Three light stabilizers were used in this study, including: (i) Lowilite 28, a benzotriazole (BTZ) ultraviolet absorber (UVA) supplied by Great Lake Chemical Corporation, (ii) Tinuvin 479, a hydroxyphenyltriazine (HPT) ultraviolet absorber supplied by Ciba, and (iii) Lowilite 62, a polymeric diester hindered amine light stabilizer (HALS) supplied by Great Lake Chemical Corporation.

Ultraviolet absorbers (UVAs) and hindered amine light stabilizers (HALS) are primarily light stabilizers for polyolefin against the UV degradation, and they have distinct protection mechanisms [28]. The protection mechanism of UVAs is based on the absorption of the UV radiation, which follows the Lambert-Beer law and depends on the amount of UVA and the thickness of stabilized-sample [28]. Thus, UVAs provide only limited protection for thin samples such as films and fibers [28]. Blocking the UV radiation passing through coating layers requires 1–5% of UVA [29]. Hydroxybenzophenone (BP), hydroxyphenylbenzotriazole (BTZ), and hydroxyphenyl-*s*-triazine (HPT) are three main classes of UVAs used commercially as photoprotective agents for polymers and coatings [28, 30]. Investigations have shown that HPT has the best photopermanence (resistant to the loss of stabilizer during the light exposure) followed by BTZ and BP [30]. Unlike UVAs, HALS do not absorb UV radiation but scavenge free radicals [31]. As a result, HALS do not rely on the thickness of the sample and relatively low concentrations (compared to those of UVAs) are required to achieve good results. When HALS is used in polyolefins, the film needs only a small amount of stabilizer (0.1–0.3%) to obtain good protection against UV radiation [31]. Combination of UVA and HALS often generates synergistic effect by enhancing the protective effect of each light stabilizer [32]. Consequently, in this study, blends of UVAs (BTZ or HPT) and HALS were incorporated into the WPC to improve its UV light resistance.

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TABLE 1. Formulations of uncapped wood-plastic composites (WPCs).

Uncapped (noncoextruded) WPC sample[a]	Amounts of ingredients (wt%)			
	BTZ	HPT	HALS	WPC
Unstabilized (control) or A1	0	0	0	100
Stabilized with BTZ/HALS blend or A2	1	0	0.3	98.7
Stabilized with HPT/HALS blend or A3	0	1	0.3	98.7

[a]Light stabilizers were added to the entire composites (bulk addition).

Compounding and Extrusion

A 20-L high intensity mixer (Papenmeier, Type TGAHK20), operated for 10 minutes, was used for room-temperature dry-blending of the $HDPE_{0.4}$ matrix, dried wood flour, and lubricant. The formulations of uncapped composites (control) and also core layer in coextruded composites contained 50% of maple flour, 44% of $HDPE_{0.4}$, and 6% of lubricant, based on the total weight of the composites. The uncapped composites were also bulk-stabilized by adding blends of UVAs and HALS in to the entire composites (Table 1).

The $HDPE_{1.2}$ was used as the polymer matrix for cap layer of coextruded composites. The $HDPE_{1.2}$ pellets were granulated and mixed with light stabilizers by using a kitchen mixer (MX1050XTS blender from Waring) for two minutes. These preblended mixtures and neat $HDPE_{1.2}$ were used as the materials for stabilized and unstabilized cap layers, respectively (Table 2).

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 publications [22–27].

Manufacture of the coextruded composites used core layers that contained $HDPE_{0.4}$/(wood flour) composites formed by 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 was 130/135/135/135°C from hopper to the coextrusion die and the rotational screw maintained a constant speed of 40 rpm throughout the processing. A 19-mm single-screw extruder (C.W. Brabender Instruments, South Hackensack, NJ) with a length-to-diameter ratio of 30:1 produced both the unstabilized and photostabilized HDPE with an MFI of (1.2 g)/(10 min) ($HDPE_{1.2}$) used as cap layers. The processing temperature profile of this extruder was 165/155/145/135°C from hopper to coextrusion die. The set temperatures and melt temperature were maintained below 200°C to minimize thermal degradation. 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 [23, 25–27].

Uncapped or noncoextruded $HDPE_{0.4}$/(wood flour) composites (control) with and without photostabilizers were also produced by using coextrusion die, in order to investigate the effect of a stabilized cap layer on the weathering of the WPCs. Manufacture of the control samples involved use of the twin screw extruder with a coextrusion die under the processing conditions similar to those mentioned above for core layers.

Accelerated Weathering Tests

The QUV weatherometer from Q-Lab Corporation housed both coextruded and noncoextruded control samples. Tests carried out according to the procedure outlined in ASTM G 154 included a 12-h cycle consisting of 8 h of UVA-340 radiation at 60°C, a 15-min water spray, and 3 h 45 min of condensation at 50°C. The UVA-340 lamps gave an excellent simulation of sunlight in the critical short wavelength region from 365 nm down to 295 nm. The UVA-340 radiation, water spray, and condensation could simulate sunlight, rain, and dew, respectively. Water spray also could introduce thermal shock and mechanical erosion.

UV-Vis Reflectance Spectroscopy

The UV-vis diffuse reflectance spectra of unstabilized and stabilized $HDPE_{1.2}$ films were obtained by using a Lambda 25 UV-vis spectrophotometer (PerkinElmer). The scans were run from 600 to 250 nm with data interval of 1 nm. The scanning speed was set at 240 nm/min.

TABLE 2. Formulations of coextruded wood-plastic composites (WPCs).

Types of cap layer on coextruded samples[a]	Amounts of ingredients (wt%)				
	Cap layer				Core layer[b]
	BTZ	HPT	HALS	$HDPE_{1.2}$	WPC
Unstabilized or B1	0	0	0	100	100
Stabilized with BTZ/HALS blend or B2	1	0	0.3	98.7	100
Stabilized with HPT/HALS blend or B3	0	1	0.3	98.7	100

[a]Light stabilizers were added to the cap layer only.
[b]The unstabilized uncapped WPC (control or sample A1) listed in Table 1 was used as core layer in coextruded composites.

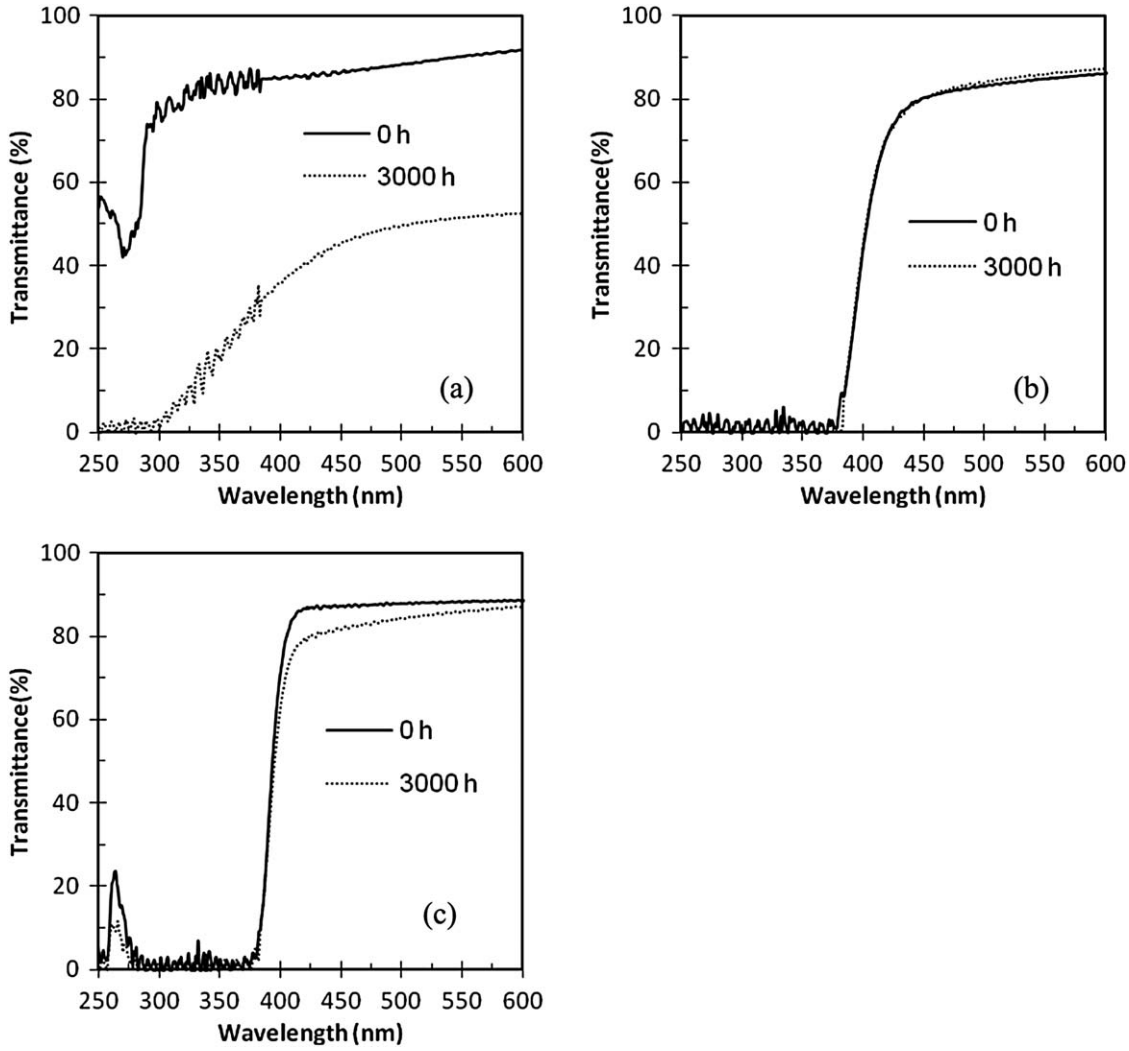

FIG. 1. UV-vis transmission spectra obtained before and after 3000 h of weathering for (a) unstabilized $HDPE_{1.2}$ film as well as $HDPE_{1.2}$ films stabilized with a combination of UVA and HALS: (b) HPT/HALS blend and (c) BTZ/HALS blend.

Scanning Electron Microscopy

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

Color Measurement

The procedure outlined in ASTM D2244 served as the means by which to perform 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 by using the Commission Internationale d'Eclairage (CIELAB 1976 color space) three-dimensional color space system. In this system, the L* axis (+L* for light, -L* for dark) represents the lightness, a* (+a* for red, -a* for green), and b* (+b* for yellow, -b* for blue) are 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 the chromaticity coordinates before and after weathering tests in order to determine the discoloration (ΔE*) of the weathered samples by using the following *Eq. [10]*:

$$\Delta E = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \quad (1)$$

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

RESULTS AND DISCUSSION

UV-Vis Reflectance Spectroscopy

Previous investigation revealed that coextruding a non-photostabilized clear hydrophobic HDPE cap layer over

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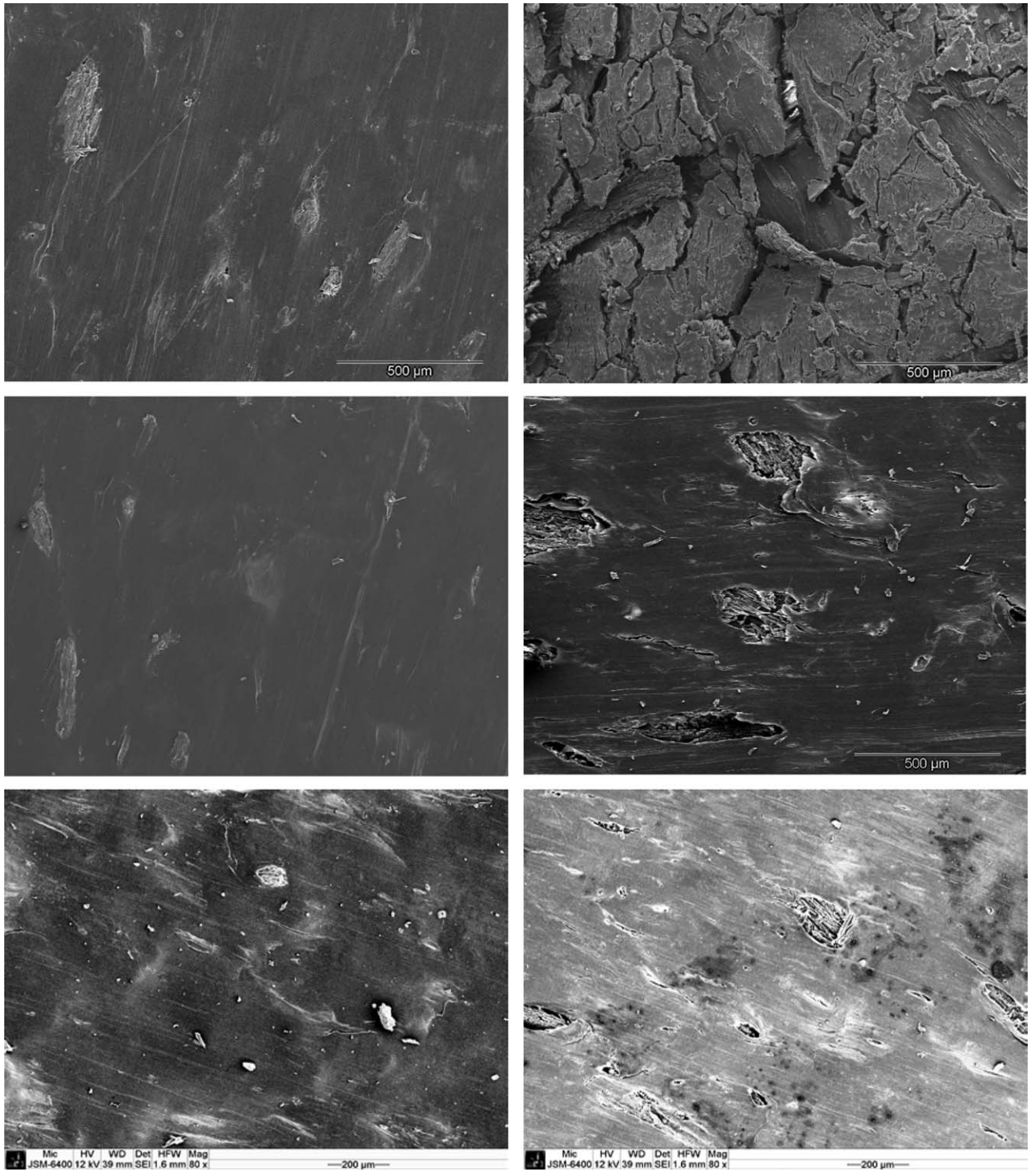

FIG. 2. SEM (×80K) micrographs of the surfaces of noncoextruded WPCs before weathering (left column) and after 3000 h of weathering (right column). Images of unstabilized WPCs are shown in the first row, whereas those with BTZ/HALS- as well as HPT/HALS-stabilized uncapped WPCs are given in the second and third rows, respectively.

WPCs failed to protect them against discoloration [27]. These results clearly implied that the clear cap layer needed photostabilization in order to protect the interface of the WPC underneath it against UV degradation. Consequently, light stabilizers were added into $HDPE_{1.2}$ films, and their effectiveness was assessed by UV-vis reflectance spectroscopy. Figure 1 shows the UV-vis reflectance spectra of unstabilized and stabilized $HDPE_{1.2}$ films before and after exposure to 3000 h of UV weathering.

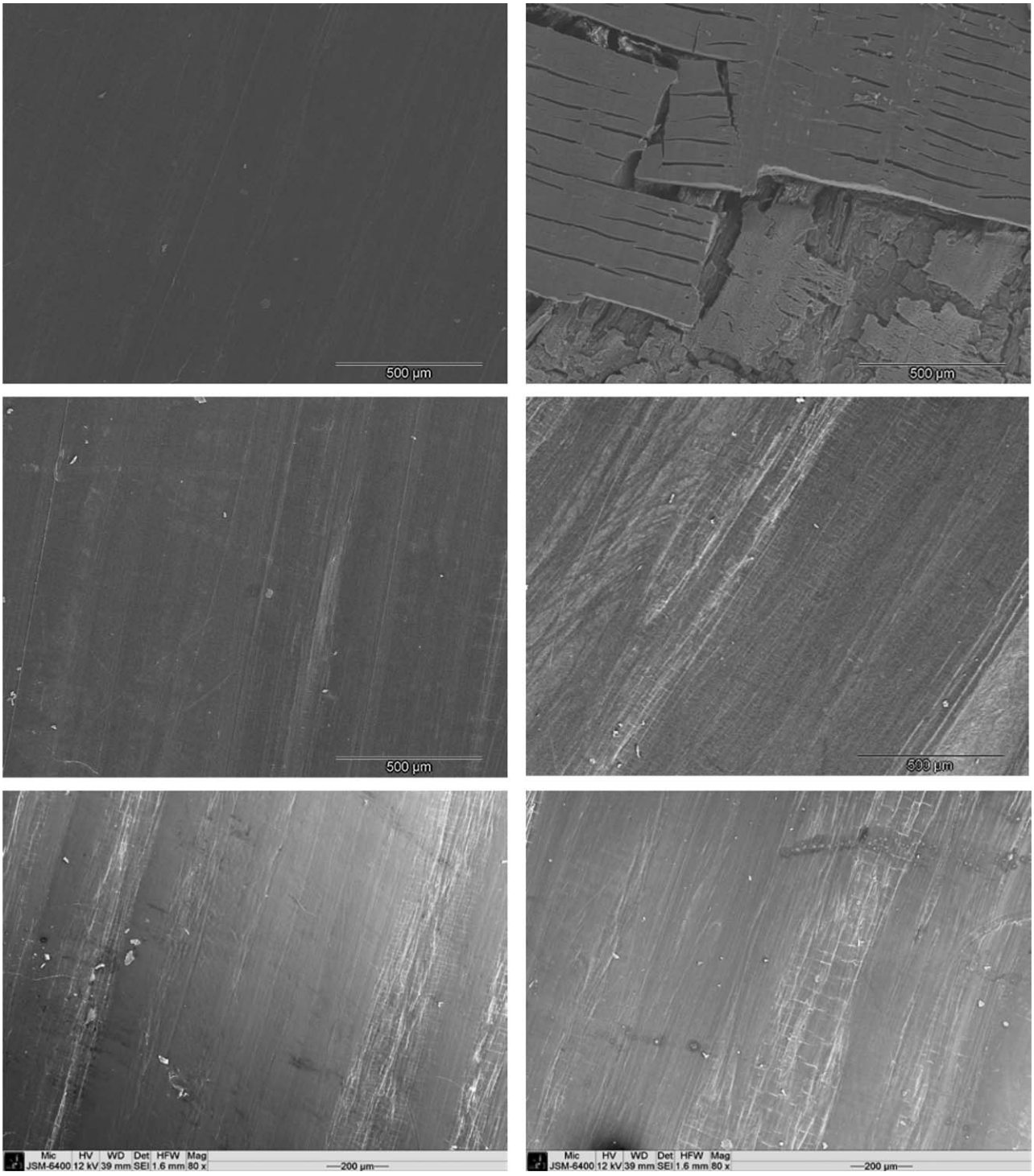

FIG. 3. SEM (×80K) micrographs of the surfaces of coextruded samples before weathering (left column) and after 3000 h of weathering (right column). Images of coextruded WPCs without light stabilizer in the cap layer are shown in the first row, while those of the counterparts with BTZ/HALS- and HPT/HALS-stabilized cap layers are shown in the second and third rows, respectively.

Before weathering (0 h), about 85% of the UV light in the UVA-340 radiation region (295–365 nm) was transmitted through the unstabilized film (Fig. 1a). By contrast, more than 95% of the UV light in this region was absorbed by the films containing light stabilizers (UVA/HALS blends) (Fig. 1b and 1c). Most importantly, photostabilization of the films did not significantly affect the light transmission in the visible region; i.e., the clarity of the films was preserved after light stabilizer addition. However, two distinct trends were seen after 3000 h of weathering. The transparency of the unstabilized film was significantly reduced in both the visible and UV regions

FIG. 4. Visual appearance of uncapped (noncoextruded) WPCs before (left column) and after exposure to 3000 h of UV weathering (right column). Images of unstabilized WPCs are shown in the first row, whereas those of BTZ/HALS- as well as HPT/HALS-stabilized uncapped WPCs appear in the second and third rows, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(Fig. 1a), a result attributed to light diffusion due to crack formation upon weathering. Conversely, stabilized films experienced only minor changes in light transmittance in both the visible and UV regions after weathering (Fig. 1b and 1c). Therefore, after 3000 h, the stabilized films still blocked more than 95% of the UVA-340 radiation without significantly affecting the light transmittance in the visible region, irrespective of the type of light stabilizer blend used. These results clearly indicate the effectiveness of UVA/HALS blends as photoprotective agents for $HDPE_{1.2}$ used as cap layer in coextruded WPCs.

Surface Morphology

Surface morphologies of noncoextruded and coextruded samples before and after 3000 h of weathering are shown in Figs. 2 and 3, respectively, where photodegradation is clearly noticeable in these images.

Prior weathering, the surfaces of uncapped WPCs (control) exhibited improper encapsulation of wood flour by the polymeric matrix in all formulations (Fig. 2, left column). After 3000 h of weathering, large cracks appeared at the surface of unstabilized formulation because of the photodegradation of the HDPE matrix and the loss of wood flour. In contrast, relatively small cracks were seen at the surfaces of stabilized formulations (Fig. 2, right column), because the light stabilizers provided photoprotection against UV radiation. The efficacy of the two light stabilizer combinations did not show significant difference.

Unlike for the uncapped WPCs (Fig. 2), the surfaces of unexposed coextruded WPCs (Fig. 3) were smoother than those of noncoextruded counterparts (Fig. 2) due to the presence of a thin HDPE cap layer on the surfaces of coextruded composites [27]. After 3000 h of weathering, large cracks and delamination of cap layer occurred at the surface of unstabilized coextruded sample (Fig. 3) due to photodegradation [27]. On the other hand, only negligible cracks, if any, appeared at the surfaces of UV-stabilized cap layers of coextruded composites, because of the presence of the light stabilizer blends, which remained effective even after 3000 h of exposure to UV light. These results corroborate the UV-vis data illustrated in Fig. 1. Once again, both light stabilizers performed similarly.

It should be pointed out that the addition method of light stabilizer into the composites appeared to have a significant effect on the photostability. Although UVA/HALS blends provided photoprotection against UV radiation, several cracks still appeared on the surfaces of stabilized uncapped composites (Fig. 2), whereas cracks were not seen on the surfaces of stabilized coextruded composites. These results imply that the addition of a light stabilizer into the bulk of a WPC is less effective for its protection against UV radiation than when it is added only at the surface of the composite.

Color Analysis

Color change is another indication of weathering. Weathering induced chemical change (the rise of chromophores) and physical changes (roughness, loss of component, etc.) result in discoloration [10–20, 26, 27]. The

FIG. 5. Visual appearance of coextruded WPC samples before (left column) and after exposure to 3000 h of UV weathering (right column). Images of coextruded WPCs without light stabilizer in the cap layer are shown in the first row, whereas the counterparts with BTZ/HALS- and HPT/HALS-stabilized cap layers are shown in the second and third rows, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

visual appearance of uncapped and coextruded composites before and after weathering is shown in Figs. 4 and 5.

Prior to exposure to UV/(water spray) cycling, the addition of light stabilizers did not affect the visual appearance of the WPCs, since both unstabilized and photostabilized WPCs had similar appearances, regardless of the stabilizer addition method used (Figs. 4 and 5). This finding was expected, since the light transmission of the HDPE film in the visible region was not affected by the addition of UVA/HALS blends, as shown by the UV-vis spectra (Fig. 1).

Both uncapped and coextruded WPCs appeared red to some extent due primarily to the addition of slightly colored wood flour into the composites (Figs. 4 and 5). Prior processing, the L^*, a^*, and b^* values of the maple flour were 54.6, 4.4, and 15.8, respectively. However, its color coordinates changed slightly when it was incorporated into both uncapped ($a^* = 5.7$ and $b^* = 16.6$) and coextruded ($a^* = 6.8$ and $b^* = 17.3$) WPCs, thus suggesting that it experienced very little thermal degradation during processing, a result which led to the slight red color in the WPCs.

Exposure to cyclic UV actions caused severe fading (lightening) of the unstabilized composites (both uncapped and coextruded WPCs) because of the photodegradation induced crack formation (Fig. 5) [27]. Nevertheless, the stabilizer addition method affected its efficacy in protecting the WPCs against UV radiation. While bulk addition of the light stabilizers into WPCs reduced the degree of fading in uncapped (control) composite, it did not suppress it completely (Fig. 4). On the other hand, coextruded composites with photostabilized cap layers showed no signs of fading, an observation clearly indicating that the stabilized cap layers on the WPCs blocked most of the UV radiation and kept UV light to reach the surface of the inner layer of coextruded composites. These results confirmed the effectiveness of UVA/HALS blends in protecting WPCs against UV degradation and corroborated the UV-vis data illustrated in Fig. 1, as well as the surface morphology shown in Figs. 2 and 3. It should also be mentioned that no significant difference between the two light stabilizer blends was observed (Fig. 4).

Quantified color parameters (Table 3) provided additional information about color changes upon weathering. Unstabilized composites experienced significant discoloration (ΔE) for both uncapped (sample A1) and coextruded (sample B1) WPCs. The increase in lightness (L^*) coupled with the decreases in both redness (a^*) and yellowness (b^*) accounted for this expected trend [12, 27]. The results are in agreement with those of our previous study that revealed the ineffectiveness of coextruding a nonphotostabilized clear hydrophobic HDPE cap layer over WPCs in order to protect the underlying WPCs against discoloration [27]. Both the nonphotostabilized cap layer and the underlying core layer experienced severe discoloration after exposure to UVA lamps at 60°C for approximately 2000 h [27]. Stabilizing the cap layer provided protection to the WPC core. After 3000 h of accelerated weathering, the discoloration (ΔE) of coextruded WPCs with photostabilized caps was only 5–6 (Table 3), with no visible damage to the cap layer (Fig. 3). In contrast, the discoloration of a coextruded WPC

TABLE 3. Color parameters of uncapped (control) and coextruded composites before and after weathering.

	L*		a*		b*		
Samples[a]	0 h	3000 h	0 h	3000 h	0 h	3000 h	ΔE
Uncapped WPCs (control)							
A1	65.6 ± 0.7	86.7 ± 0.6	5.7 ± 0.2	1.1 ± 0.1	16.6 ± 0.2	3.1 ± 0.0	26.1 ± 1.3
A2	68.1 ± 0.7	77.0 ± 1.7	5.6 ± 0.0	3.9 ± 0.7	16.4 ± 0.1	12.0 ± 1.1	11.0 ± 0.8
A3	67.8 ± 0.4	76.6 ± 1.1	5.6 ± 0.1	4.1 ± 0.5	16.3 ± 0.2	13.4 ± 0.6	9.4 ± 1.1
Coextruded WPCs							
B1	57.9 ± 1.5	85.3 ±0.9	6.8 ±0.5	0.0 ± 0.2	17.3 ± 1.0	8.9 ± 1.5	29.1 ± 1.4
B2	56.7 ± 0.8	60.6 ± 1.1	6.7 ± 0.2	8.0 ± 0.1	15.8 ± 1.3	20.0 ± 1.6	5.8 ± 0.6
B3	57.8 ± 1.0	60.9 ± 2.0	6.2 ± 0.2	7.6 ± 0.7	15.6 ± 0.5	18.3 ± 1.8	4.9 ± 0.9

[a]The descriptions of samples are listed in Tables 1 and 2 for uncapped WPCs and coextruded WPCs, respectively.

with a nonphotostabilized cap was 6.2 after only 192 h of accelerated weathering and visible damage was observed after only 744 h [27].

Generally, photostabilized WPCs underwent less discoloration than their unstabilized counterparts (Table 3) for both uncapped and coextruded samples. Discoloration of coextruded composites was attributed to the increases in lightness, redness, and yellowness; whereas the increases in lightness combined with the decreases in both redness and yellowness accounted for the discoloration of uncapped composites.

Overall, stabilized uncapped WPCs experienced more discoloration than coextruded ones, confirming the efficacy of adding light stabilizers at the surface of the composites. Once again, there was no significant difference between two light stabilizer combinations in protecting the WPCs against UV radiation.

Cost Analysis Considerations

Generally, the amount of each ingredient in the formulations must be known to estimate the cost of a product. This amount could be obtained by estimating the total weight of a WPC, which could be achieved by determining its volume. The following calculations provide material compositions for cost considerations in order to evaluate the options of adding light stabilizers into the bulk of WPCs or only at the cap layer of coextruded WPCs.

First, let us assume that a 0.0254-m × 0.1524-m × 3.6576-m (1-in × 6-in cross-section × 144 in long) uncapped WPC is manufactured on the basis of the formulation in Table 1. For uncapped composite (control), light stabilizer is added into the entire WPCs. The volume and weight of this uncapped WPC will be 1.416×10^{-2} m^3 and 12.6 kg, respectively if its density is 890 kg/m^3 [3].

Second, let us assume that a WPC is capped with a 0.2 mm thin $HDPE_{1.2}$ layer [23, 27] based on the formulation of Table 2. If this coextruded WPC has the same dimensions as the uncapped counterpart, then the width and thickness of the WPC in the core are each reduced by 0.4 mm, while its length remains constant at 3.6576 m (144 in). Composite in the core layer will have a volume of 1.39×10^{-2} m^3. Consequently, the volume of the $HDPE_{1.2}$ cap layer is estimated to be 2.60×10^{-4} m^3, which is the difference between the volumes of uncapped WPC and the WPC core layer. The weight of $HDPE_{1.2}$ used as cap layer will be 0.25 kg, since its density is 960 kg/m^3.

The amounts of each ingredient in the WPCs calculated from the above mentioned weight values are listed in Table 4 for both uncapped and coextruded composites. While the amounts of HDPE, wood flour, and lubricant used in both the uncapped and coextruded WPCs remained almost the same (ratios of these ingredients in uncapped and coextruded WPCs ranged from 0.97 to 1.0), more of the light stabilizers (50 times) were needed when they were incorporated into the bulk of the composites rather than in the cap layer. These results clearly suggest that adding light stabilizers at the surface of WPCs not only protects them against UV degradation, but also is more efficient and cost-effective than the bulk addition method. Because the protective additives are only added to the cap layer of coextruded WPCs instead of the entire composites, stabilized coextruded composites save the materials cost as compared to that of stabilized uncapped composites.

CONCLUSIONS

We evaluated the effect of the method of addition of light stabilizer into wood-plastic composite [only at surface (or cap layer) versus into the entire composites (or bulk addition)] on its photo stability. Blends of ultraviolet absorbers (UVAs) (benzotriazole or hydroxyphenyltriazine) with a hindered amine light stabilizer (HALS) were used as light stabilizers. Both unstabilized and photostabilized uncapped (control) as well as coextruded wood-plastic composite (WPC) counterparts were exposed up to 3000 h of accelerated artificial weathering. The light transmittance, surface morphology, and color of the

TABLE 4. Amounts of ingredients in wood-plastic composites for cost analysis considerations.

Ingredient	Amount (kg)[a]		Ratio of uncapped/ coextruded WPC
	Uncapped WPC	Coextruded WPC	
$HDPE_{0.4}$	6.2200	6.1850	0.97[b]
$HDPE_{1.2}$	—	0.2468	—
Wood flour	5.4736	5.4428	1.0
Lubricant (TPW104)	0.7464	0.7422	1.0
UVA (BTZ or HPT)	0.1260	0.0025	50.4
HALS	0.0378	0.00078	50.4

[a]The weight percentages of ingredients are given in Tables 1 and 2.
[b]The total amount of HDPE in coextruded WPCs includes both $HDPE_{0.4}$ and $HDPE_{1.2}$.

samples before and after weathering were analyzed by UV-vis spectroscopy, SEM, and Chroma Meter. The following conclusions were drawn from the experimental results:

After 3000 h of exposure to UV/(water spray) cycling, the stabilized $HDPE_{1.2}$ films used as cap layer still blocked more than 95% of UVA-340 radiation without significantly affecting the light transmittance in the visible region, irrespective of the type of light stabilizer blend used. These results clearly indicated the efficacy of UVA/HALS blends as photoprotective agents for $HDPE_{1.2}$ used as cap layer in coextruded WPCs.

The addition method of light stabilizer into the composites had a significant effect on photostability. Morphology study showed that although UVA/HALS blends provided photo-protection against UV radiation, several cracks still appeared on the surfaces of stabilized uncapped composites (control), whereas cracks were not seen on the surfaces of stabilized coextruded composites. These findings were supported by the visual appearance and color evaluation of the samples. While bulk addition of light stabilizers into WPCs reduced the degree of fading in uncapped (control) composites, it did not suppress it completely. On the other hand, coextruded composites with photostabilized cap layers showed no visible signs of fading, thus clearly indicating that the stabilized cap layers on WPCs blocked most of the UV radiation of UVA-340 lamps, thereby preventing UV light to reach the surface of the inner layer of coextruded composites. Overall, stabilized uncapped WPCs experienced more discoloration than coextruded ones. The results clearly suggested that the addition of light stabilizers into the bulk of WPCs was less effective for their protection against UV radiation than when the stabilizers were added only at the surface of the composites. There was no significant difference between the two light stabilizer combinations in protecting the WPCs against UV radiation.

Cost analysis considerations indicated that more light stabilizer (50 times) was needed when it was incorporated into the bulk of the composites rather than in the cap layer of coextruded samples. Clearly, these results suggested that adding light stabilizers at the surface of WPCs not only protected them against UV degradation, but also was a more efficient and cost-effective method for photostabilization of the composites than bulk addition.

In this paper, we manufactured coextruded composites with a WPC core and a stabilized HDPE cap layer. In such composites, migration of stabilizers from the cap layer into an HDPE-based core may reduce their efficiency. This effect may be magnified under less accelerated weathering conditions. In uncapped WPCs, stabilizers are present in the HDPE matrix, fiber/polymer interface, and porous areas in the wood fiber. The loss of stabilizers from the fiber/polymer interface or porous areas in the fiber would reduce their long-term performance. Therefore, in future studies the migration and loss of stabilizers needs to be considered when designing a photostabilized formulation.

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