Ultraviolet Weathering of Photostabilized Wood-Flour-Filled High-Density Polyethylene Composites

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ABSTRACT: Wood–plastic composites are being increasingly examined for nonstructural or semistructural building applications. As outdoor applications become more widespread, durability becomes an issue. Ultraviolet exposure can lead to photodegradation, which results in a change in appearance and/or mechanical properties. Photodegradation can be slowed through the addition of photostabilizers. In this study, we examined the performance of wood flour/high-density polyethylene composites after accelerated weathering. Two 2^4 factorial experimental designs were used to determine the effects of two hindered amine light stabilizers, an ultraviolet absorber, a colorant, and their interactions on the photostabilization of high-density polyethylene blends and wood flour/high-density polyethylene composites. Color change and flexural properties were determined after 250, 500, 1000, and 2000 h of accelerated weathering. The results indicate that both the colorant and ultraviolet absorber were more effective photostabilizers for wood flour/high-density polyethylene composites than the hindered amine light stabilizers. © 2003 Wiley Periodicals, Inc.* J Appl Polym Sci 90: 2609–2617, 2003

Key words: polyethylene (PE); mechanical properties; degradation; composites

INTRODUCTION

Although inorganic fillers currently dominate the thermoplastic industry, wood-derived fillers have become more accepted in recent years. The use of wood fibers in plastics is expected to increase by 50% through 2005, to a great extent as a result of the recent acceptance of wood–plastic composites (WPCs) into the construction industry for applications such as decking, siding, roofing tiles, and window frames.[1]

The use of WPCs by the construction industry has resulted in concern about the durability of these products exposed to outdoor environments. Outdoor durability may include thermal stability, moisture resistance, fungal resistance, and ultraviolet (UV) stability. Articles have been published about the susceptibility of WPCs to moisture and fungal attack,[2–4] the photodegradation of WF-filled poly(vinyl chloride) composites,[5,6] and the photodegradation of wood-flour-filled polyethylene (WF/PE) composites.[7,8]

Falk et al.[7] investigated the color fading of WF/PE and polypropylene composites after accelerated weathering. The results indicated that the polypropylene-based composites faded more than the polyethylene (PE)-based composites. These researchers also determined that colorants could be used to effectively lessen the color fading of WF/PE composites after accelerated weathering but that a hindered amine light stabilizer (HALS) did not protect against color fading. However, the stabilization mechanism of the ineffective HALS added by itself was not addressed. In addition, the effect of combining a colorant and HALS is not known. Lundin[8] weathered photostabilized WF/PE composites and monitored the degradation of the mechanical properties. The composites lost 33% stiffness after 2000 h of weathering. However, because a composite without the photostabilizer was not monitored, the effect of the photostabilizer was not known. Despite this initial work, a fundamental understanding of the photostabilization of WF/PE composites is lacking.

The photodegradation of WPCs is a difficult problem, complicated by the fact that each component may degrade via a different mechanism. The photodegra-

TABLE I
Materials and Content of the Composite Blends

Variable	Supplier	Trade name	Content (%)
WF	American Wood Fibers	4020	50
LS1	Ciba Specialty Chemicals	Tinuvin 770 DF	0, 0.5
LS2	Ciba Specialty Chemicals	Chimassorb 944 FD	0, 0.5
UVA	Ciba Specialty Chemicals	Tinuvin 328	0, 0.5
Color	Holland Colors Americas, Inc.	Cedar TI-8536	0, 1
HDPE	Solvay Polymers, Inc.	Fortiflex A60-70-162	47.5–50

dation of polyolefins originates from excited polymer–oxygen complexes[9] and is caused mainly by the introduction of catalyst residues, hydroperoxide groups, carbonyl groups, and double bonds during polymer manufacturing. Even in the absence of a significant amount of UV absorption, small amounts of these impurities can be sufficient to induce polymer degradation.[10] Degradation of polymers as a result of photooxidation has undesirable effects, including a loss of strength, stiffness, and surface quality. Slowing down or stopping the reactions that are responsible for degradation is necessary for UV stabilization.

Photostabilizers are compounds developed to combat UV degradation. They are generally classified according to the degradation mechanism they hinder. Ultraviolet absorbers (UVAs), hydroperoxide decomposers, and free-radical scavengers are all important photostabilizers for polyolefins. Commercial UVAs are readily available as benzophenones and benzotriazoles.[10] A relatively new class of materials, HALSs, has been extensively examined for polyolefin protection[11,12] as free-radical scavengers. Although hydroperoxides can act as photoinitiators, the concentration of hydroperoxides in PE drops quickly on UV exposure.[10]

The individual components of wood—cellulose, hemicellulose, lignin, and extractives—are variously susceptible to photodegradation.[13] Research has shown that the weathering of wood is confined to the wood surface and involves photo-induced breakdown of lignin to water-soluble reaction products, which leads to the generation of chromophoric functional groups such as carbonyls, carboxylic acids, quinones, and hydroperoxy radicals.[13] Coating the wood surface inhibits photodegradation by limiting UV absorption.

Although the photodegradation of both PE and wood have been extensively examined, little information is available on the photodegradation of wood-flour-filled high-density polyethylene (WF/HDPE) composites.[7,8] In addition, much of the available information on photostabilizers covers solely the photostabilization of unfilled plastics.[9–12] The results of the study reported here will aid in the development of an understanding of how photostabilizers affect the properties of WF/HDPE composites after weathering. This study had two main objectives: (1) to characterize the optical and mechanical properties of weathered high-density polyethylene (HDPE) blends and 50% WF/HDPE composites and (2) to determine the effectiveness of various photostabilizers and their interactions on the weathering of WF/HDPE composites.

EXPERIMENTAL

Materials

The materials used in this study are presented in Table I. Combinations of wood flour (WF), a hydroxy benzotriazole UVA, a low-molecular-weight HALS (LS1), a high-molecular-weight HALS (LS2), and zinc ferrite in a carrier wax (Color) were added to HDPE. In each blend to which WF was added, the WF was maintained at 50 wt % of the composite, whereas the photostabilizers and HDPE constituted the remainder of the composite. The effects of each variable on the color and flexural properties and their interactions were determined with a 2^4 factorial experimental design.

Processing

The hygroscopic WF was dried for 24 h at 105°C to remove moisture before being dry-blended with the additives and HDPE. Compounding was accomplished with a 32-mm Davis Standard (Pawcatuck, CT) corotating twin-screw extruder to produce homogeneous composite pellets. The melt temperature varied between 385 and 400°C. All of the composite pellets were dried at 105°C for at least 24 h before they were injection-molded. Test specimens were molded in a 33-ton Cincinnati Milacron (Batavia, OH) reciprocating-screw injection molder. The nozzle temperature was set to 400°C. The ASTM mold cavity used for the flexural samples was $120 \times 3 \times 12$ mm.[14]

Testing and analysis

Weathering

Twenty replicates of each of 32 formulations were placed in a xenon arc-type light exposure apparatus operated according to ASTM D 2565.[14] Samples were mounted in four rows on a drum that rotated around the xenon arc bulb at 1 rpm. The samples were rotated
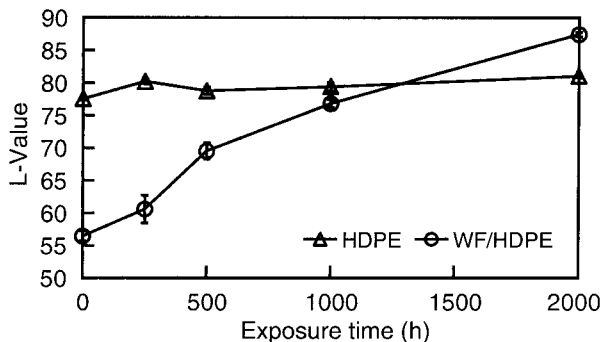
Figure 1 Effect of exposure time on *L* of unfilled HDPE and WF/HDPE composites.
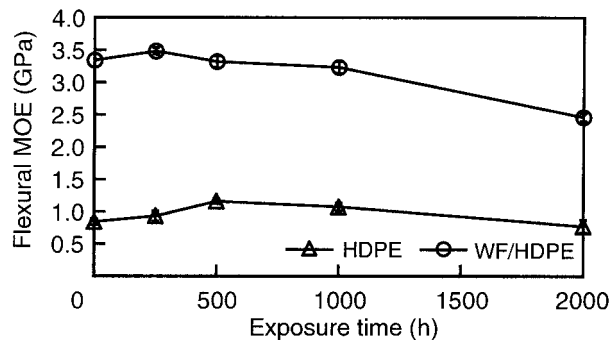

Figure 2 Effect of exposure time on flexural MOE of unfilled HDPE and WF/HDPE composites.

periodically to ensure that all were exposed to the same irradiance. The exposure cycle consisted of 108 min of light exposure and 12 min of simultaneous water spray and light exposure.[14] To understand the initial effect of UV exposure, we removed samples for analysis after 250, 500, 1000, and 2000 h of exposure.

Optical properties

A Minolta CR-200 Chroma Meter (Minolta Corp., Ramsey, NJ) was used to measure color with the CIELAB color system. Lightness (*L*) and chromaticity coordinates (*a* and *b*) were measured for five replicate samples, and the color change (ΔE_{ab}) was determined with the procedure outlined in ASTM D 2244:[15]

$$\Delta E_{ab} = (\Delta L^2 + \Delta a^2 + \Delta b^2)^{1/2} \qquad (1)$$

where ΔL, Δa, and Δb represent the differences between the initial and final values of *L*, *a*, and *b*, respectively. In the CIELAB color system, the value *L* can be thought of as a lightness factor. An increase in *L* means the sample is lightening (i.e., a positive ΔL for lightening and a negative ΔL for darkening). A positive Δa signifies a color shift toward red, and a negative Δa signifies a color shift toward green. A positive Δb signifies a shift toward yellow, and a negative Δb signifies a shift toward blue.

Mechanical properties

Samples were oven-dried at 105°C for 24 h before testing. This ensured the same conditioning for samples before and after exposure. Flexural tests were carried out according to ASTM D 790[14] on an Instron universal testing machine. The three-point loading system was used with a crosshead speed of 1.3 mm/min. The exposed surface was placed away from the center load to place that part of the sample in tension. At least four replicate specimens were tested for each formulation. The stress at maximum load and tangent

modulus of elasticity (MOE) were calculated according to the standard.

Statistics

To determine the effects of weathering on the mechanical properties, a two-tailed *t* test was carried out at an α value of .05 to compare the exposed data to the unexposed data. An attempt was made to model each property in terms of LS1, LS2, UVA, and Color after 2000 h of exposure with a full factorial statistical analysis. In this type of design, selected variables are tested at different levels.[16] Experiments are run on all combinations of variables and levels. In this study, the effects of two levels (added or not added to the blend) on four variables resulted in 16 formulations for both HDPE blends and WF/HDPE composites. This was accomplished with Design Expert 6.0.0 software by Stat-Ease, Inc. (Minneapolis, MN). If the data could be characterized with full factorial analysis, that is, if we were able to generate a model describing the data, the derived equations are reported in terms of coded factors. Coding reduces the range of each factor to a common scale, −1 to 1, regardless of its relative magnitude. In typical coding, −1 is the lower level of a factor, and 1 is the upper level.[16]
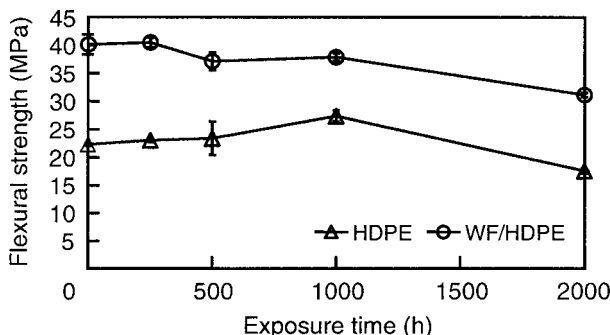

Figure 3 Effect of exposure time on flexural strength of unfilled HDPE and WF/HDPE composites.

TABLE II
ΔE_{ab} and ΔL at Various Exposure Times for Unfilled HDPE and Photostabilizer Blends After Accelerated Weathering

Photostabilizer				ΔE_{ab} exposure time (h)				ΔL exposure time (h)[a]			
LS1	LS2	UVA	Color	250	500	1000	2000	250	500	1000	2000
−	−	−	−	4.6	4.5	4.5	4.9	2.6	1.2	1.8	3.5
+	−	−	−	1.9	10.5	11.5	11.0	0.7	3.2	3.4	3.8
−	+	−	−	8.4	9.7	9.9	9.5	−1.7	2.8	2.5	3.4
−	−	+	−	2.6	3.2	4.0	4.5	2.3	1.3	1.5	1.8
−	−	−	+	0.5	2.4	3.0	3.2	−0.4	0.1	−0.1	0.1
+	+	−	−	4.0	11.4	11.9	11.4	−0.6	3.5	3.7	4.2
+	−	+	−	4.1	6.7	7.7	7.8	−0.8	1.9	2.5	3.1
−	+	+	−	9.2	6.6	7.4	6.9	−3.5	2.3	2.1	2.7
+	−	−	+	0.3	1.4	1.8	2.7	0	−0.2	−0.4	−0.1
−	+	−	+	0.5	2.7	2.8	3.4	0.1	0.3	0.3	0.3
−	−	+	+	0.9	1.7	2.0	1.6	0.3	0.1	−0.3	0.3
+	+	+	−	8.0	7.4	8.4	7.8	−3.0	3.3	3.2	3.8
+	+	−	+	0.5	2.9	3.7	4.3	−0.4	−0.2	−0.3	−0.2
+	−	+	+	0.2	1.2	2.7	4.1	0.1	−0.3	−0.4	−0.4
−	+	+	+	0.9	1.7	2.5	1.1	0.1	−0.3	−0.3	0.3
+	+	+	+	0.2	2.5	3.6	3.8	−0.2	−0.1	−0.1	0.2

[a] One standard deviation for $L = 0.3$.

RESULTS AND DISCUSSION

Figures 1–3 present the data obtained for the L value, flexural MOE, and flexural strength of the blends without photostabilizers at different exposure times. Each error bar corresponds to one standard deviation. In Tables II–V, columns 1 through 4 indicate the types of photostabilizer added to each composite blend. A plus sign designates that the photostabilizer was included in the blend, and a minus sign designates the absence of the photostabilizer. The data in the first row are for the formulation without photostabilizers. The effects of individual photostabilizers are shown in rows 2 to 5; the effects of combining two to four photostabilizers are shown in rows 6 through 16. In

Tables IV and V, boldfaced and underlined values represent no significant change in properties from unexposed values at $\alpha = .05$.

For each aspect of the study, the discussion is presented in two parts: (1) the performance of unfilled HDPE blends and (2) the performance of WF/HDPE composites.

Color analysis

Unfilled HDPE blends

Table II shows the values of ΔE_{ab} and ΔL at different exposure times for HDPE blends without WF. The calculated total ΔE_{ab} typically increased with increas-

TABLE III
ΔE_{ab} and ΔL at Various Exposure Times for WF/HDPE and Photostabilizer Blends After Accelerated Weathering

Photostabilizer				ΔE_{ab} exposure time (h)				ΔL exposure time (h)[a]			
LS1	LS2	UVA	Color	250	500	1000	2000	250	500	1000	2000
−	−	−	−	4.4	16.7	25.4	35.8	4.1	13.1	20.4	31.0
+	−	−	−	8.6	20.2	29.3	37.2	8.0	17.5	25.2	33.1
−	+	−	−	9.0	19.6	28.1	34.7	8.6	16.4	23.6	30.5
−	−	+	−	6.7	17.7	25.6	32.8	5.7	13.6	20.1	27.7
−	−	−	+	6.6	13.1	20.1	25.4	6.2	11.4	18.6	24.3
+	+	−	−	7.9	19.4	27.6	34.8	7.7	17.2	24.2	31.5
+	−	+	−	7.4	18.2	27.0	33.8	7.2	16.3	23.7	30.5
−	+	+	−	6.9	16.3	24.7	30.3	6.6	13.9	20.8	26.8
+	−	−	+	7.1	13.3	18.7	23.6	6.9	12.6	17.9	22.7
−	+	−	+	9.6	16.4	21.6	26.1	9.4	15.6	20.8	25.2
−	−	+	+	5.7	11.1	16.0	20.8	5.5	9.8	14.7	19.7
+	+	+	−	8.3	18.6	25.9	32.2	8.1	16.9	23.1	29.4
+	+	−	+	11.7	17.8	23.6	27.5	11.4	17.1	22.8	26.7
+	−	+	+	7.8	13.1	19.2	23.8	7.7	12.3	18.3	22.9
−	+	+	+	10.8	15.0	20.9	26.0	10.7	14.4	20.1	25.2
+	+	+	+	7.1	14.4	19.6	23.8	6.9	13.8	18.8	22.9

[a] One standard deviation for $L = 1.1$.

TABLE IV
Change in Flexural MOE and Strength at Various Exposure Times for Unfilled HDPE and Photostabilizer Blends After Accelerated Weathering

Photostabilizer				MOE (GPa) exposure time (h)					Strength (MPa) exposure time (h)				
LS1	LS2	UVA	Color	0	250	500	1000	2000	0	250	500	1000	2000
−	−	−	−	0.84	**0.93**	1.16	1.07	**0.77**	22.3	23.0	**23.4**	17.1	17.5
+	−	−	−	0.80	0.90	0.93	1.10	0.93	21.6	24.9	25.3	27.4	27.2
−	+	−	−	0.89	**0.96**	1.00	1.14	1.03	22.7	26.1	26.6	28.9	28.1
−	−	+	−	0.79	0.90	0.90	1.05	1.01	21.5	24.3	25.8	27.8	27.3
−	−	−	+	0.81	1.00	0.98	1.12	0.97	21.3	25.1	25.9	27.4	25.6
+	+	−	−	0.81	0.98	0.94	1.12	1.03	21.5	24.9	25.7	28.0	26.7
+	−	+	−	0.78	0.91	0.91	1.07	0.88	20.9	23.9	24.9	27.4	26.5
−	+	+	−	0.74	0.95	0.96	1.08	1.07	21.2	24.7	25.4	27.2	27.5
+	−	−	+	0.81	0.99	0.96	1.10	0.99	21.0	25.2	25.3	28.0	25.3
−	+	−	+	0.87	1.01	1.01	1.16	1.03	22.3	25.7	26.3	28.7	26.8
−	−	+	+	0.80	0.90	0.96	1.11	0.98	22.0	24.8	25.3	27.7	25.3
+	+	+	−	0.74	0.92	0.88	1.07	0.98	20.3	24.4	24.3	27.7	25.9
+	+	−	+	0.78	0.96	0.92	1.13	0.92	20.6	24.8	25.5	28.4	25.8
+	−	+	+	0.79	0.94	0.88	1.07	0.91	19.6	24.6	24.2	27.1	25.1
−	+	+	+	0.85	0.98	1.03	1.14	**0.97**	21.8	25.7	26.7	28.6	24.6
+	+	+	+	0.72	0.92	0.90	1.07	0.96	19.9	24.0	24.7	27.4	25.0

Boldfaced and underlined values represent no significant change in properties from unexposed values at $\alpha = .05$.

ing exposure time. At 2000 h, samples without colorant (Color) had larger ΔE_{ab} values than samples with colorant. The determination of total ΔE_{ab} took into account the three color parameters: L, a, and b. If ΔL were the most important parameter influencing total ΔE_{ab}, the trend of ΔL would follow that of ΔE_{ab}. A diversion of the ΔL from the ΔE_{ab} trend would typically indicate a change resulting from the yellowing of the sample $(+\Delta b)$ through the initial weathering stages. After 2000 h of exposure, HDPE samples with colorant generally showed little, if any, lightening after UV exposure regardless of the presence of other photostabilizers. This trend was similar to that observed for ΔE_{ab}. The derived equation describing the relationship between the change in lightness factor after 2000 h of exposure (ΔL_{2000h}) and the various photostabilizers (in terms of coded factors) supports the relative importance of both colorant and UVA in preventing the lightening of neat HDPE samples:

$$\Delta L_{2000h} = 1.66 + 0.12(LS1) + 0.16(LS2)$$
$$- 0.21(UVA) - 1.62(Color)$$
$$- 0.31(LS1)(Color) + 0.23(UVA)(Color) \quad (2)$$

$$\text{Predicted } r^2 = 0.96$$

TABLE V
Change in Flexural MOE and Strength at Various Exposure Times for WF/HDPE and Photostabilizer Blends After Accelerated Weathering

Photostabilizer				MOE (GPa) exposure time (h)					Strength (MPa) exposure time (h)				
LS1	LS2	UVA	Color	0	250	500	1000	2000	0	250	500	1000	2000
−	−	−	−	3.34	3.48	**3.32**	**3.23**	2.46	40.1	**40.5**	37.2	37.9	31.2
+	−	−	−	3.35	**3.40**	**3.29**	**3.32**	2.49	41.1	**40.4**	**39.0**	**39.3**	34.0
−	+	−	−	3.34	**3.38**	**3.20**	3.15	2.58	41.3	**40.5**	**39.9**	38.9	34.6
−	−	+	−	3.01	3.19	**3.11**	3.24	2.47	37.6	**37.5**	**38.4**	**38.5**	33.7
−	−	−	+	3.51	3.91	**3.37**	3.60	2.98	38.3	**38.2**	**37.4**	**37.1**	34.4
+	+	−	−	3.42	**3.48**	**3.33**	**3.33**	2.71	41.0	**40.8**	**40.7**	**39.9**	35.8
+	−	+	−	3.34	**3.33**	**3.24**	**3.42**	2.42	39.7	**39.1**	**39.0**	**39.9**	34.9
−	+	+	−	3.24	**3.27**	**3.11**	**3.32**	2.44	39.4	**38.7**	**38.5**	**39.0**	35.2
+	−	−	+	3.80	**3.83**	**3.59**	**3.72**	3.20	39.8	**40.1**	**39.4**	**39.5**	36.3
−	+	−	+	3.81	**3.82**	**3.67**	**3.73**	3.20	38.7	**38.4**	**38.5**	37.4	35.7
−	−	+	+	3.41	**3.45**	**3.38**	3.66	**3.31**	36.2	**37.5**	**37.3**	**37.6**	**34.2**
+	+	+	−	3.28	**3.33**	3.07	**3.23**	2.62	40.3	39.2	**38.5**	37.7	36.3
+	+	−	+	3.94	**3.97**	**3.63**	3.72	3.09	39.1	**38.9**	**38.5**	**37.6**	36.2
+	−	+	+	3.72	**3.71**	**3.38**	**3.82**	3.08	37.2	**38.6**	**37.3**	**37.4**	34.8
−	+	+	+	3.45	3.64	**3.36**	3.69	3.11	37.5	**36.2**	**38.0**	**38.4**	34.9
+	+	+	+	3.76	3.57	**3.35**	**3.59**	3.08	37.6	**38.3**	**37.7**	**38.7**	36.2

Boldfaced and underlined values represent no significant change in properties from unexposed values at $\alpha = .05$.
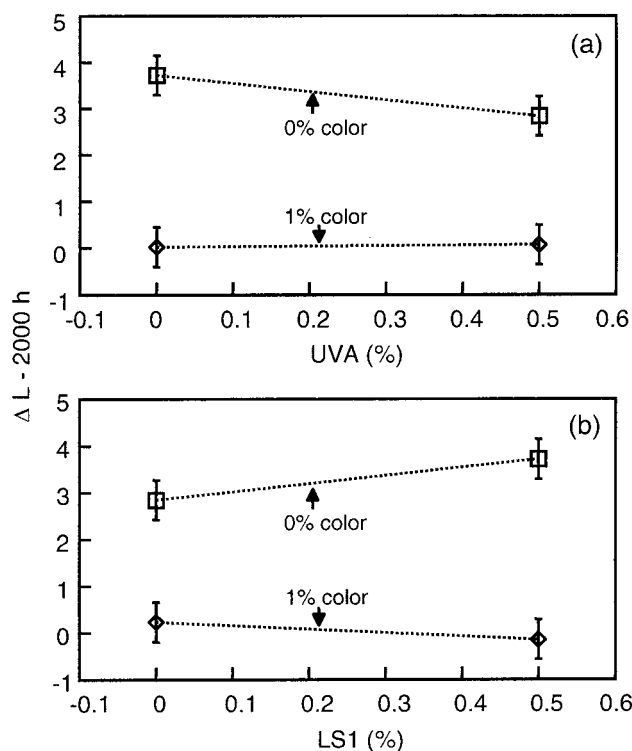
Figure 4 Variation in ΔL as function of the interactions between colorant and photostabilizer: (a) contents of LS1 and LS2 fixed at 0.25% and (b) contents of LS2 and UVA fixed at 0.25%.

All of the main effects (LS1, LS2, UVA, and Color) and the significant two-factor interaction (LS1/color and UVA/color) are included in eq. (2). The relative effect of each factor in this equation is expressed by its coefficient and algebraic sign.[16] As eq. (2) clearly indicated, the colorant (Color) and UVA were the two most important photostabilizers that prevented lightening of the HDPE blends [negative algebraic sign in eq. (2)]. Color, however, had a more pronounced effect than UVA, as suggested by its coefficient value (i.e., 1.62 for Color compared with 0.21 for UVA). In contrast, the addition of HALSs (LS1 and LS2) did not prevent lightening [positive algebraic sign in Eq. (2)].

Despite significant interactions (LS1/Color and UVA/Color), the colorant did not exert a large synergistic effect. This is shown clearly in Figure 4, which shows ΔL as a function of the interactions between UVA and Color [Fig. 4(a)] and LS1 and Color [Fig. 4(b)]. These graphs represent the data and model described in eq. (2). The strong dependence of ΔL on Color content was apparent. The value of ΔL significantly decreased when Color content increased at 0 or 0.5% of LS1 or UVA. These results imply that the colorant used in the formulation was the most effective photostabilizer for preventing the lightening of unfilled HDPE.

WF/HDPE composites

For WF/HDPE composites, it was apparent that both ΔE_{ab} and ΔL increased with increasing exposure time (Table III). Although all of the samples experienced a significant increase in L, the increase was less pronounced if the colorant was a component of the formulation. The only photostabilizers to significantly lower ΔL were UVA and Color , as shown by the negative coefficients. As with the results for the unfilled HDPE composites, the most influential photostabilizer for color fading was the colorant (Color). Interestingly, eq. (3) contains neither an LS1 or LS2 term, implying that HALSs alone or in combination did not have a significant effect on the ΔL of the composites. This is explained in the next section:

$$\Delta L_{2000h} = 26.86 - 1.26(\text{UVA}) - 3.19(\text{Color}) \quad (3)$$

$$\text{Predicted } r^2 = 0.75$$

In comparing the ΔE_{ab}'s of the unfilled HDPE blends (Table II) and the WF/HDPE composites (Table III), it was clear to us that the magnitude of lightening was much greater for the composites (Fig. 1). At 2000 h, ΔL ranged from −0.4 to 4.2 for unfilled PE blends. The corresponding ΔL for WF/HDPE composites ranged from 19.7 to 33.1. Addition of WF to HDPE clearly had a negative effect on color fading.

These results suggest that the majority of the color fading of composites may be due to a bleaching of the wood fibers. The addition of UVA can be used to absorb some UV radiation before the wood is exposed and bleached. However, UVAs are ineffective in protecting polymer films.[17] In injection-molded fiber-filled samples, a polymer film is present at the surface.[18] Although the addition of UVA to WF/HDPE composites significantly lowered ΔL from 31.0 to 27.7, this value was, nevertheless, much higher than the value obtained for unfilled HDPE blends. The addition of a colorant to block the penetration of UV radiation and to mask the bleaching of WF was more effective than the addition of UVA, which lowered ΔL to 24.3. The combination of UVA and colorant provided the best protection, lowering ΔL to 19.7.

Flexural property analysis

Tables IV and V summarize the flexural properties of unfilled HDPE blends and WF/HDPE composites, respectively. Flexural MOE was calculated with the initial tangential slope of the load–displacement curve, and flexural strength was calculated with the maximum load sustained by the sample. All the samples failed on the tensile side during testing.

Unfilled PE blends

For unfilled HDPE samples, flexural MOE and strength generally changed significantly on exposure after as little as 250 h (Table IV). For many formulations, MOE appeared to increase with increasing exposure time through 1000 h. After 2000 h, MOE was lower than that reported at 1000 h but was, nevertheless, higher than that of the unexposed samples for all of the blends except unprotected HDPE. Although the full factorial analysis showed that no significant factors influenced MOE of HDPE after 2000 h of exposure, the data indicated that the photostabilizers provided some level of protection (Table IV).

As with flexural MOE, the strength of unfilled HDPE blends increased through 1000 h of exposure and then dropped off slightly at 2000 h of exposure (Fig. 2), regardless of the addition of photostabilizer (Table IV). Despite this decrease, all of the UV-exposed samples, except for unprotected HDPE, showed greater flexural strength values than did their unexposed counterparts, even after 2000 h of exposure. The photostabilizers or combinations were not significantly different in regard to the change in strength of HDPE at 2000 h of exposure.

This phenomenon is explained by changes in the polymer morphology. Tidjani et al. (2000) exposed low-density polyethylene (LDPE) to both natural and accelerated weathering and examined the elongation at break in conjunction with the formation of carbonyl and vinyl groups after weathering. They determined that in the initial stages of accelerated weathering, the mechanisms of degradation result in a predominance of crosslinking reactions over chain scission.[19] In a later study, Tidjani expanded on this explanation,[20] concluding that the crosslinking that occurs after accelerated weathering reduces the concentration of radicals that take part in the oxidation process. This was supported by experimental evidence that a high elongation at break was retained during the initial stages of exposure. The author suggested that a relatively high level of oxidation was necessary to overcome crosslinking and decrease elongation.[20]

A complementary explanation came from Jabarin and Lofgren,[21] who also examined the structural changes of HDPE after natural and accelerated weathering. They reported an increase in the concentration of carbonyl and vinyl compounds, an increase in crystallinity, and a decrease in molecular weight after natural weathering.[21] They determined that as PE undergoes photooxidation during the course of UV exposure, chain scission occurs, as evidenced by an increase in the concentration of carbonyl and vinyl groups and a decrease in molecular weight. These authors concluded that shorter chains have higher mobility and crystallize readily, resulting in an apparent increase in crystallinity.[21] As UV exposure continues, chain scission continues to affect molecular weight and crystallinity, which leads to the embrittlement of the PE, which corresponds with a decreased elongation at break.[21] Kaci et al. also reported an increase in the crystallinity of LDPE after natural weathering.[22]

In our case, the PE blends were exposed to accelerated weathering. We think that crosslinking and chain scission occurred simultaneously at later stages but that crosslinking dominated initially. Initial crosslinking may have hindered the chain mobility, resulting in an increase in strength and modulus. For the unprotected PE blend, maximum properties were observed at approximately 500 h of exposure (Table IV). After 500 h, chain scission became the more influential structural change, which led to a drop in mechanical properties. After 2000 h, there was no net change in flexural MOE, and there was a net drop in flexural strength. The photostabilizers and colorant may have been effective in delaying the switch from crosslinking to chain scission by absorbing or blocking UV radiation and scavenging free radicals. Therefore, the degradation of properties was delayed. Further research is being conducted to verify the proposed mechanisms of degradation. The maximum properties were observed around 1000 h after exposure. After 2000 h of exposure, a drop in properties became apparent, but there was still a net increase in properties relative to those of unexposed samples. We expect that the degradation of properties of all of the HDPE blends would continue with increasing exposure time.

WF/HDPE composites

The change in the flexural MOE of weathered WF/HDPE composites compared with the flexural MOE of unexposed composites was generally insignificant until the exposure time reached 2000 h (Fig. 3, Table V). Others have indicated similar trends. After 4000 h of weathering, Lundin[8] found that WF/HDPE composites retained only 45% preexposure MOE. However, more than 35% stiffness loss occurred in the first 1000 h of exposure. Unlike the flexural MOE of unfilled HDPE blends, flexural MOE values of most WF/HDPE composites exposed to 2000 h UV were significantly lower than that of their unexposed counterparts. These results imply that addition of WF to PE was detrimental to the retention of MOE after accelerated weathering. The only blend that did not experience a significant decrease in MOE was the WF/HDPE composite with UVA and colorant. The full factorial statistical analysis at 2000 h, however, led us to conclude that the change in MOE was unaffected by photostabilizer type.

Similar to the trend observed for the flexural MOE of WF/HDPE composites, flexural strength generally did not change significantly until the exposure time

reached 2000 h. At this point, a drop in strength occurred that was most extreme for the unprotected WF/HDPE composite. Both colorant and UVA significantly decreased the loss in strength compared with that of the unprotected composite . The derived regression equation describing the relationship between the change in flexural strength after 2000 h of UV exposure and various photostabilizers (in terms of coded factors) is as follows:

$$\Delta\text{Strength} = [36.45 + 9.83(\text{UVA})$$
$$+ 15.53(\text{Color})]^{1/2} - 9.87 \quad (4)$$

$$\text{Predicted } r^2 = 0.84$$

An examination of eqs. (3) and (4) showed that for the WF/HDPE composites, both LS1 and LS2 did not significantly change color fading or loss in flexural strength. The ineffectiveness of HALSs may be attributed to the acid acceptor characteristic of wood. The amine group on each HALS acts as an electron donor (base). As a result, the basic HALS will react with any acidic component.[17] The parameters K_A (acceptor) and K_D (donor) can be used to characterize a material as an electron acceptor or donor. These values were determined for 60/80-mesh eastern white pine. It was reported that if extractives were removed from the wood, as might occur during composite processing, the K_A and K_D would be 0.15 and 0.11, respectively.[23] This leads one to the conclusion that the surface of the wood acts as an electron acceptor and can undergo an acid–base interaction with the HALS, thus affecting the performance of the light stabilizer.

Unlike unfilled HDPE blends, WF/HDPE composites did not experience a change in properties immediately, but they did experience a net loss in properties after 2000 h of exposure (Table V). This may have been due to moisture sorption during weathering. The samples cycled through environments of 35°C and 100% relative humidity during the water spray cycle, and 40°C and 30% relative humidity during the dry cycle. Moisture has been shown to affect the properties of wood–polymer composites. Stark[2] examined the effects of moisture on the flexural properties of 40% WF/PE composites. Composites exposed to 30% relative humidity for 2000 h experienced no loss in flexural properties. However, composites exposed to a water bath for 2000 h experienced a 39% loss in flexural modulus and a 22% loss in flexural strength.[2]

In the initial stages of the weathering of the HDPE/WF composites, the loss of properties caused by moisture exposure may have cancelled out the gain resulting from polymer crosslinking. This would explain the observed plateau during the first 1000 h of exposure. At 2000 h, a substantial decrease in properties occurred. It was at this point that the HDPE prop-

erties may have been degrading as a result of chain scission and moisture. For unprotected HDPE/WF composites, this corresponded with a 26% drop in MOE and a 22% drop in strength, partly as a result of a loss in interfacial strength.[2] Unlike unfilled HDPE composites, WF/HDPE composites experienced a net loss in flexural MOE and strength after weathering for 2000 h. The UVA and colorant provided some protection against strength loss . However, they may have protected the polymer only and may not have influenced the drop in strength properties because of moisture exposure.

In addition, WF undergoes photodegradation, resulting in the breakdown of lignin to form free radicals.[13] The free radicals may attack the PE chain, resulting in the deleterious effect of the addition of WF to PE through an accelerated chain scission in the PE. Indeed, the loss of flexural MOE of the WF/HDPE composite without additives was almost double that of the loss in MOE of the HDPE composite (26% versus 12%). These results suggest that both the loss of interfacial quality and photodegradation of WF contribute to the loss of flexural strength and stiffness of WF/HDPE composites.

CONCLUSIONS

As WPCs become increasingly used for outdoor applications, a need to understand their UV durability arises. There is little fundamental information available on the photostabilization of WF/HDPE composites. In this study, a full factorial experimental design was used to examine the effects of photostabilizers on both unfilled HDPE blends and WF/HDPE composites. Optical and flexural properties were examined for all of the formulations after they had been exposed to UV light in an accelerated weathering apparatus. Our analysis led to the following conclusions:

1. The lightening effect was decreased through the addition of a UVA and colorant for both unfilled HDPE blends and WF/HDPE composites. However, because of the bleaching of the WF, WF/HDPE composites experienced more dramatic lightening than the unfilled HDPE blends.
2. After 2000 h of laboratory UV exposure, unprotected HDPE blends experienced a drop in flexural strength and MOE, which could be mitigated through the addition of a photostabilizer.
3. The flexural properties (both MOE and strength) of HDPE blends were immediately affected by UV exposure, whereas the flexural properties of WF/HDPE composites were not significantly affected until 2000 h of exposure. The addition of UVA and a colorant significantly decreased strength loss.

4. HALSs did not have a significant effect on the *L* and flexural properties of the WF/HDPE composite formulations tested. This was due to acid–base interactions resulting from the acid-sensitive hindered amines and the acidic characteristics of the WF.

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