

PHOTOSTABILIZATION OF WOOD FLOUR FILLED HDPE COMPOSITES

*Nicole M. Stark, Forest Products Laboratory, Madison, WI 53705
Laurent M. Matuana, Michigan Technological University, Houghton, MI 49931*

Abstract

Wood/plastic composites are increasingly examined for non-structural building applications. As outdoor applications become more widespread, durability becomes an issue. Ultraviolet exposure can lead to photodegradation, resulting in a change in appearance and/or mechanical properties. Photodegradation can be slowed through the addition of photostabilizers. This study examines the performance of photostabilized HDPE/wood flour composites after accelerated weathering. A full factorial experimental design was used to determine the effects of hindered amine light stabilizers (HALS), a W absorber (UVA), a colorant, and their interactions on the photostabilization of the composite. After 250, 500, 1000, and 2000 hours of accelerated weathering, color change and flexural properties were determined. The experimental results indicate that both colorant and UVA are more effective photostabilizers for wood flour/HDPE composites than HALS.

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 due largely in part to the recent acceptance of wood/plastic composites (WPC) into the construction industry for applications such as decking, siding, roofing tiles, and window frames (1).

The use of WPC by the construction industry has resulted in concern about the durability of WPC exposed to outdoor environments. Outdoor durability may include thermal stability, moisture uptake, fungal resistance, and ultraviolet (UV) stability. Although articles have been published on the durability of WPC (2-5), the information available on the photodegradation of wood flour filled polyethylene (PE) composites is sparse (6). Photodegradation of WPC is a difficult problem complicated by the fact that each component may degrade via different mechanisms.

The photodegradation of polyolefins originates from excited polymer-oxygen complexes (7) and is caused mainly by the presence of catalyst residues, hydroperoxide groups, carbonyl groups, and double bonds introduced during polymer manufacturing. Even in the absence of a significant amount of W absorption, small amounts of these impurities can be sufficient to induce degradation of the polymer (8). Degradation of polymers

due to photooxidation has such undesirable effects as loss of strength, stiffness, and surface quality. Slowing down or stopping the reactions that are responsible for degradation is necessary for UV stabilization.

Compounds developed to protect polyolefins and combat UV degradation, photostabilizers, are generally classed according to the degradation mechanism they hinder. Ultraviolet absorbers (UVA), quenchers, hydroperoxide decomposers, and free radical scavengers are all important photostabilizers for polyolefins. Commercial UVAs also act as quenchers (8), and a relatively new class of materials, hindered amine light stabilizers (HALS) have been extensively examined for polyolefin protection (9,10) as free radical scavengers. Hydroperoxide decomposers have been found to be unimportant in the protection of polyethylene (8).

Similarly, wood undergoes photodegradation. The individual components of wood; cellulose, hemicellulose, lignin, and extractives, are all susceptible to photodegradation (11). Research has shown that the weathering of wood is a process that is confined to the surface of the wood, involving photo-induced breakdown of lignin to water-soluble reaction products. This leads to the generation of chromophoric functional groups such as carbonyls, carboxylic acids, quinones, hydroperoxy radicals, etc. (11). Coating the surface of wood often disrupts the degradation process.

Although the photodegradation of both PE and wood have been extensively examined, little information on the photodegradation of wood flour filled high-density polyethylene (HDPE) composites is available. In addition, much of the available information on photostabilizers covers solely the photostabilization of unfilled plastics. The results of this project will aid in the development of an understanding of the effect photostabilizers on the properties of wood flour/HDPE composites after weathering. This study has two main objectives: 1) to characterize the optical and mechanical properties of weathered wood flour/HDPE composites, and 2) to determine the effectiveness of various photostabilizers and their interactions on the weathering of wood flour/HDPE composites.

Methods

Materials

The materials used in this study are presented in Table 1. Combinations of wood flour (WF) and

photostabilizers were added to HDPE. In each case, the wood flour was maintained at 50% by weight of the composite, while the photostabilizers and HDPE constituted the remainder of the composite. The effects of each of the variables on properties, as well as their interactions, were determined using a full-factorial experimental design with five variables, resulting in 32 blends.

Processing

The wood flour was dried for 24 hours at 105°C, and then dry-blended with the additives and HDPE at the composition required to generate each composite. Compounding was accomplished using a 32-mm Davis Standard (Pawcatuck, CT) co-rotating, intermeshing, 32:1 length to diameter ratio, twin-screw extruder to produce homogeneous composite pellets. All composite pellets were dried at 105°C for at least 24 hours prior to injection molding. Test specimens were molded in a 33-ton Cincinnati Milacron reciprocating screw injection molder (Batavia, Ohio). The American Society for Testing and Materials mold cavity used for the flexural samples is 120 x 3 x 12 mm (ASTM D790).

Testing and Analysis

Weathering. Twenty replicates of each of the 32 formulations were placed in a xenon arc-type light-exposure apparatus and operated according to ASTM D2565 (12). Samples were mounted on a drum that rotated around the chamber at 1 rpm, in four rows. The samples were rotated periodically to ensure that all samples were exposed to the same irradiance. The exposure cycle consisted of 108 minutes of light exposure and 12 minutes of simultaneous water spray and light exposure. Samples were removed after 250, 500, 1000, and 2000 hours of exposure for analysis.

Optical Properties. A Minolta CR-200 Chroma Meter was used to measure color using the CIELAB color system. L, a and b were measured for five replicate samples and color change, ΔE_{ab} , was determined (Eqn. 1) using the procedure outlined in ASTM D2244 (12). In the CIELAB color system, the value L can be thought of as a lightness factor, positive b represents yellow, negative b represents blue, positive a represents red, and negative a represents green.

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

Mechanical Properties. The samples were oven-dried at 105 °C for 24 hours before testing. This ensured the same conditioning for samples before and after exposure. Flexural tests were carried out according to ASTM D790 on an Instron Universal Testing (12). The three point loading system was utilized 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 were calculated according to the standard.

Results and Discussion

Color Analysis

In Tables 2-5, columns A, B, C, and D represent the photostabilizer added to each composite blend. A plus sign "+" designates that the photostabilizer is included in the blend whereas a minus sign "-" designates the absence of the photostabilizer. The first row shows the formulation without photostabilizers. In the next four rows, the effects of the individual photostabilizers can be seen while the effect of combining two to four of the photostabilizers can be seen in rows six through sixteen. A value reported in gray italics represents no significant change in property at $\alpha = 0.05$. An attempt was made to model each property in terms of LS1, LS2, UVA, and Color.

Optical Properties. Table 2 shows ΔE_{ab} and ΔL and at different exposure times for the PE composites without the addition of wood flour. Generally, the HDPE samples that had the Color added showed little if any change in lightness after UV exposure regardless of the other photostabilizers added. In the absence of Color, the UVA performed the best at 2000 hours exposure time. It was determined that UVA, Color, and a LS1/Color interaction all significantly lower the ΔL for the photostabilized HDPE formulations (Eqn. 2).

$$\Delta L = 1.66 + 0.12 * LS1 - 0.21 * UVA - 1.62 * Color - 0.31 * LS1 * Color + 0.23 * UVA * Color \quad (2)$$

Predicted $r^2 = 0.94$

It is apparent that both ΔE_{ab} and ΔL increase with increasing exposure time for all photostabilized wood flour/HDPE composites (Table 3). Examining the results for ΔL , it is evident that while all samples experiences a significant increase in ΔL , the increase less pronounced if Color is a component of the formulation. As with the HDPE formulations, at 2000 hours of exposure time the UVA performed the best in the absence of Color. The only photostabilizers to significantly lower ΔL are UVA and Color (Eqn. 3).

$$\Delta L = 26.86 - 1.26 * UVA - 3.19 * Color \quad (3)$$

Predicted $r^2 = 0.75$

Mechanical Properties. The flexural MOE and strength generally changed significantly for the HDPE formulations upon exposure starting as early as 250 hours of exposure time (Table 4). For many of the formulations,

the MOE appears to increase with increasing exposure time through 1000 hours. At this point the MOE drops off slightly. There are no significant factors that influence the MOE for photostabilized HDPE at 2000 hours exposure time.

The strength for HDPE without the addition of photostabilizers decreases after 1000 hours of exposure time (Table 4). All of the photostabilizers used negated this effect and even increased the change in strength due to W exposure. As with the flexural MOE, the strength of the photostabilized formulations increases through 1000 hours of exposure time and then drops off slightly. None of the photostabilizers or combinations perform significantly different from one another regarding the change in strength of HDPE at 2000 hours exposure time.

The change in flexural MOE is generally insignificant for wood flour/HDPE composites until the exposure time reaches 2000 hours (Table 5). At this point there is a decrease in MOE. The change in MOE appears unaffected by the addition of photostabilizers.

Similar to the trend seen for the flexural MOE of wood flour/HDPE composites, the flexural strength generally does not change significantly until the exposure time reaches 2000 hours. At this point, there is a drop in strength that is most extreme for the unprotected wood flour/HDPE formulation. The addition of Color improves the drop in strength over the unprotected formulation. Again in the absence of Color, the UVA performed the best at 2000 hours of exposure time. Both Color and UVA significantly increase the strength (Eqn 4).

$$\Delta Str. = \left(\frac{36.45 + 9.83 * UVA + 15.53 * Color}{\text{Predicted } r^2 = 0.84} \right)^{\frac{1}{2}} - 9.87 \quad (4)$$

Summary

As wood plastic composites become increasingly used for outdoor applications, a need to understand their UV durability arises. There is little available information regarding the photostabilization of wood flour/HDPE composites. In this study, a full-factorial experimental design was used to examine the effects of photostabilizers on both unfilled HDPE and wood flour/HDPE composites. Optical and flexural properties were examined for all the formulations after they had been exposed to UV in an accelerated weathering apparatus. After analysis, the following statements can be made:

- 1) The change in ΔL is decreased through the addition of UVA and Color for both unfilled HDPE and wood flour/HDPE.
- 2) The effect of HALS on ΔL is not significant for any of the formulations.
- 3) The flexural properties of HDPE are immediately affected by UV exposure while the properties of wood flour/HDPE composites are not affected until 2000 hours of exposure.
- 4) Exposure of unprotected HDPE results in a drop in flexural strength, which can be reversed through the addition of any of the photostabilizers.
- 5) The strength of wood flour/HDPE composites decreases upon UV exposure at 2000 hours, and UVA and Color both significantly increase the change in strength.

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Variable		Suppliers	Tradename	Content (%)
Wood Flour	WF	American Wood Fibers	4020	50
Low MW Light Stabilizer	HALS-1	Ciba Specialty Chemicals	Tinuvin 770 DF	0.5
High MW Light Stabilizer	HALS-2	Ciba Specialty Chemicals	Chimassorb 944 FD	0.5
Ultraviolet Absorber	UVA	Ciba Specialty Chemicals	Tinuvin 328	0.5
Colorant	Color	Holland Colors Americas, Inc.	Cedar TI-8536	1
High-Density Polyethylene	HDPE	Solvay Polymers, Inc.	Fortiflex A60-70-162	47.5-50

Table 2. ΔE_{ab} and ΔL at various exposure times for unfilled HDPE and photostabilizer blends.

A HALS1	B HALS2	C UVA	D Color	ΔE_{ab} ExposureTime(Hours)				ΔL ExposureTime(Hours)			
				250	500	1000	2000	250	500	1000	2000
-	-	-	-	4.59	4.51	4.53	4.88	2.63	1.22	1.81	3.45
+	-	-	-	1.86	10.54	11.46	11.01	0.69	3.22	3.41	3.83
-	+	-	-	8.39	9.68	9.92	9.53	-1.74	2.82	2.46	3.40
-	-	+	-	2.60	3.22	4.04	4.46	2.28	1.31	1.47	1.80
-	-	-	+	0.48	2.44	3.00	3.15	-0.36	0.06	-0.08	0.12
+	+	-	-	4.04	11.41	11.85	11.40	-0.56	3.45	3.69	4.20
+	-	+	-	4.10	6.72	7.73	7.78	-0.82	1.91	2.52	3.07
-	+	+	-	9.25	6.58	7.39	6.94	-3.53	2.32	2.08	2.73
+	-	-	+	0.27	1.40	1.83	2.72	0.04	-0.17	-0.35	-0.15
-	+	-	+	0.52	2.66	2.80	3.36	0.13	0.32	0.27	0.27
-	-	+	+	0.91	1.67	2.03	1.64	0.31	0.06	-0.31	0.27
+	+	+	-	7.97	7.42	8.41	7.79	-2.99	3.28	3.21	3.75
+	+	-	+	0.48	2.90	3.68	4.32	-0.44	-0.20	-0.25	-0.17
+	-	+	+	0.22	1.20	2.68	4.07	0.09	-0.28	-0.41	-0.43
-	+	+	+	0.91	1.72	2.50	1.08	0.11	-0.34	-0.31	0.26
+	+	+	+	0.21	2.51	3.55	3.80	-0.16	-0.05	-0.10	0.16

Table 3. ΔE_{ab} and ΔL at various exposure times for wood flour filled HDPE and photostabilizer blends.

A HALS1	B HALS2	C UVA	D Color	ΔE_{ab} ExposureTime(Hours)				ΔL ExposureTime(Hours)			
				250	500	1000	2000	250	500	1000	2000
-	-	-	-	4.35	16.67	25.39	35.84	4.14	13.07	20.37	31.01
+	-	-	-	8.60	20.24	29.29	37.19	7.98	17.50	25.17	33.11
-	+	-	-	9.04	19.55	28.06	34.70	8.57	16.45	23.60	30.48
-	-	+	-	6.73	17.66	25.57	32.82	5.72	13.56	20.08	27.65
-	-	-	+	6.63	13.12	20.07	25.41	6.22	11.36	18.62	24.25
+	+	-	-	7.94	19.41	27.58	34.78	7.67	17.23	24.15	31.53
+	-	+	-	7.42	18.20	27.05	33.80	7.24	16.34	23.73	30.47
-	+	+	-	6.86	16.30	24.74	30.29	6.61	13.85	20.80	26.76
+	-	-	+	7.07	13.26	18.69	23.60	6.94	12.62	17.95	22.67
-	+	-	+	9.60	16.38	21.65	26.13	9.42	15.57	20.75	25.21
-	-	+	+	5.67	11.09	16.01	20.82	5.48	9.79	14.66	19.66
+	+	+	-	8.34	18.61	25.91	32.17	8.11	16.86	23.12	29.37
+	+	-	+	11.65	17.76	23.56	27.55	11.43	17.11	22.81	26.67
+	-	+	+	7.84	13.06	19.21	23.84	7.70	12.35	18.33	22.87
-	+	+	+	10.79	14.95	20.86	26.02	10.66	14.44	20.08	25.17
+	+	+	+	7.15	14.42	19.60	23.80	6.93	13.84	18.79	22.90

A HALS 1	B HALS 2	C UVA	D Color	Δ MOE (GPa)				Δ Strength(MPa)			
				Exposure Time (hours)				Exposure Time (hours)			
				250	500	1000	2000	250	500	1000	2000
-	-	-	-	0.09	0.31	0.22	-0.07	0.74	1.11	-5.21	-4.76
+	-	-	-	0.10	0.13	0.30	0.13	3.24	3.63	5.73	5.51
-	+	-	-	0.07	0.10	0.25	0.14	3.40	3.88	6.18	5.37
-	-	+	-	0.11	0.11	0.27	0.22	2.75	4.29	6.30	5.79
-	-	-	+	0.19	0.18	0.32	0.17	3.77	4.54	6.12	4.25
+	+	-	-	0.17	0.14	0.31	0.22	3.46	4.21	6.51	5.25
+	-	+	-	0.13	0.13	0.29	0.10	2.97	3.97	6.48	5.57
-	+	+	-	0.22	0.23	0.34	0.33	3.52	4.21	6.01	6.33
+	-	-	+	0.18	0.15	0.28	0.18	4.12	4.22	6.98	4.30
-	+	-	+	0.14	0.14	0.29	0.16	3.38	3.98	6.42	4.51
-	-	+	+	0.11	0.16	0.31	0.18	2.82	3.32	5.66	3.28
+	+	+	-	0.18	0.14	0.33	0.23	4.18	4.06	7.44	5.61
+	+	-	+	0.18	0.14	0.35	0.14	4.22	4.93	7.79	5.16
+	-	+	+	0.15	0.09	0.28	0.12	4.99	4.58	7.42	5.51
-	+	+	+	0.13	0.18	0.28	0.12	3.86	4.86	6.83	2.82
+	+	+	+	0.20	0.17	0.35	0.24	4.03	4.77	7.42	5.05

Table 5. Flexural modulus and strength at various exposure times for wood flour filled HDPE and photostabilizer blends.

A HALS 1	B HALS 2	C UVA	D Color	Δ MOE (GPa)				Δ Strength (MPa)			
				Exposure Time(hours)				Exposure Time (hours)			
				250	500	1000	2000	250	500	1000	2000
-	-	-	-	0.14	-0.01	-0.10	-0.87	0.39	-2.99	-2.25	-8.97
+	-	-	-	0.06	-0.06	-0.03	-0.85	-0.65	-2.04	-1.79	-7.10
-	+	-	-	0.05	-0.13	-0.18	-0.75	-0.76	-1.37	-2.36	-6.69
-	-	+	-	0.19	0.10	0.24	-0.53	-0.11	0.80	0.84	-3.90
-	-	-	+	0.41	-0.13	0.10	-0.52	-0.13	-0.89	-1.18	-3.88
+	+	-	-	0.06	-0.08	-0.09	-0.70	-0.18	-0.27	-1.01	-5.19
+	-	+	-	-0.01	-0.10	0.08	-0.93	-0.64	-0.76	0.19	-4.87
-	+	+	-	0.03	-0.13	0.08	-0.80	-0.64	-0.85	-0.33	-4.21
+	-	-	+	0.03	-0.21	-0.08	-0.60	0.31	-0.41	-0.27	-3.48
-	+	-	+	0.01	-0.14	-0.09	-0.61	-0.29	-0.23	-1.37	-3.03
-	-	+	+	0.16	0.08	0.37	0.02	1.34	1.12	1.41	-2.01
+	+	+	-	0.05	-0.21	-0.06	-0.67	-1.09	-1.77	-2.61	-4.02
+	+	-	+	0.03	-0.31	-0.22	-0.85	-0.22	-0.58	-1.53	-2.88
+	-	+	+	-0.01	-0.35	0.10	-0.65	1.48	0.12	0.28	-2.35
-	+	+	+	0.19	-0.09	0.24	-0.34	-1.28	0.46	0.88	-2.61
+	+	+	+	-0.18	-0.41	-0.16	-0.68	0.70	0.12	1.12	-1.36

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