Effect of Weathering Variables on the Lightness of High-Density Polyethylene Woodflour Composites

Nicole M. Stark

Abstract

Wood-plastic lumber is promoted as a low-maintenance, high-durability product. After weathering, however, wood-plastic composites (WPCs) often fade. In the first part of this study, 50 percent woodflour-filled high-density polyethylene (HDPE) composite samples were manufactured. Composites were exposed to two accelerated weathering cycles in a xenon-arc type weathering apparatus: either ultraviolet (UV) light only or UV light and water spray. The composites lightened less when they were exposed to only W light compared with exposure to UV light and water spray. In the second part of this study, WPCs with changing wood contents were exposed to UV radiation with water spray. The results were compared with exposure to both a single water soak and a series of cyclical soaking-drying periods. Composites exposed to a single water soak did not lighten, those exposed to cyclical soaking and drying lightened only at high wood contents, and all composites lightened after exposure to UV radiation with water spray. The results of this study demonstrate that exposing WPCs to water spray in combination with UV light is more severe than exposing WPCs to only UV light, or to only water. This is likely a result of water spray washing away the degraded layer and wood extractives during weathering, as well as causing the wood-plastic interface to be compromised through dimensional changes in wood particles.

Stark:

Chemical Engineer, USDA Forest Service, Forest Products Lab., Madison, WI, USA

Introduction

Wood-derived fillers have made inroads into the thermoplastic industry, primarily as wood-plastic composites (WPCs) become more prevalent in construction applications. Exterior building products, such as decking, fencing, siding, window framing, and roof tiles, are currently available or being introduced into the market.

Wood-plastic lumber is promoted as a low-maintenance, high-durability product (1). However, use of WPCs by the construction industry has resulted in concern about durability of these products after weathering. Several papers report weathering characteristics of polyethylene (PE)-based WPCs. When exposed to accelerated weathering, WPCs often fade (2-4).

There are many competing degradation mechanisms that occur during WPC weathering, and both ultraviolet (UV) radiation and moisture exposure can be detrimental. Exposure to UV radiation can result in changes in the polymer matrix as well as changes in the wood component. Photodegradation of PE results in free radical generation, which may then lead to termination via cross-linking or chain scission. While cross-linking and chain scission are competitive mechanisms of UV degradation, it has been shown that cross-linking is preferred during accelerated weathering (5). Chain scission can result in more chain mobility and secondary recrystallization. The result of photodegradation is surface cracking, and a loss in strength and stiffness. Wood also undergoes photodegradation. Lignin at the surface of wood is primarily degraded, leaving a cellulose rich surface. As wood undergoes photodegradation, the cellulose rich, oxidized surface becomes more wettable (6).

WPCs are detrimentally affected by the presence of moisture primarily due to the wood component. Wood is a naturally hydrophilic material. As a result, wood cell walls swell when penetrated by water, facilitating light penetration further into wood, providing sites for further degradation (7), and removing some water soluble extractives. In WPCs, the swelling wood fiber compromises the wood/matrix interface and creates microcracks in the matrix. The result is a change in appearance and destruction of mechanical properties.

In current literature, a change in properties of WPCs after accelerated weathering is often reported after a given exposure time (2-4). However, during accelerated weathering measured variables can include exposure time, UV exposure as radiant energy over a specific wavelength range, and water exposure as number of cycles or time. Using only exposure time as a means of comparison between studies may be meaningless if the intensity of UV exposure and amount of water exposure are not known. Each weathering variable must be consistent before comparing results from different studies. To allow for better comparison between studies, it is recommended that performance after weathering be reported after a specific radiant exposure, the time integral of irradiance (8). In current WPC weathering literature, radiant exposure is often not known, and amount of water exposure may not be reported, therefore comparisons between studies are often not possible.

It is not known how primary weathering variables influence color fade of WPCs. This is knowledge that would help us to understand and identify methods for protecting WPCs from fading. The main objective of this study was to understand how exposing WPCs to two weathering variables, UV radiation and water, independently and together lighten woodflour-filled HDPE composites. As a secondary objective, it was important to conduct the exposures so that comparison between them was meaningful.

Experimental Methods

This study consisted of two phases during which unstabilized WPCs were subjected to different exposures. In the first phase, WPCs were exposed to UV radiation with water spray and compared with composites exposed to UV radiation only. In the second phase, WPCs were again exposed to UV radiation with water spray but compared with composites soaked in water. During each phase, lightness of WPCs was analyzed before and after exposure.

Materials

The materials used in the first phase were wood flour and high-density polyethylene (HDPE). The wood flour was 40-mesh ponderosa pine supplied by American Wood Fibers (AWF 4020, Schofield, WI, USA). The HDPE was virgin material with a melt index of 0.72 g/10 minutes and density of 0.963 g/cm^3 (Fortiflex A60-70-162, Solvay Polymers, Inc., Houston, TX, USA). The wood flour was 50 percent by weight of the composite.

In the second phase, wood flour content was varied from 0 to 60 percent by weight of the composite. The same wood flour was used as the first phase. The HDPE was a virgin material with a melt index of 5 g/10 minutes and a density of 0.948 g/cm^3 (HD 6605, Exxon Mobil, Houston, TX, USA).

Injection molded

Wood flour was dried for 24 hours at 105°C. HDPE and wood flour were compounded using a 32-mm Davis Standard (Pawcatuck, CT, USA) twin-screw extruder with a strand die to produce homogeneous woodflour-HDPE composite pellets. The pellets were dried at 105°C for at least 24 hours prior to injection molding into flexural bar test samples. Composites were injection molded, using a 33-ton Cincinnati Milacron (Batavia, OH, USA) injection molder, into bars that were 120 by 3 by 12 mm.

Testing

Weathering

Composite samples were placed in a xenon arc-type exposure apparatus with inner and outer borosilicate filters. The xenon-arc bulb has a spectral radiation distribution similar to solar radiation. Therefore, UV, visible, and infrared portions of the spectrum were all present during the radiation period. However, UV radiation is the most damaging to composites therefore the exposure is referred to as exposure to UV radiation in this paper. Composites were exposed to UV radiation or UV radiation and water spray. Samples were mounted on a drum that rotated around the xenon arc bulb at 1 rpm. For samples exposed to UV radiation only, exposure was continuous. If a water spray cycle was used, a 2-hour cycle consisting of 108 minutes UV radiation and 12 minutes simultaneous water spray and UV radiation was followed. In both cases, an irradiance sensor was used to measure light intensity for UV wavelengths from 300 to 400 nm (XenoCal, Atlas Materials Testing Technology, Linsengericht, Germany). Irradiance was monitored and voltage to the

Table 1. ~ *Weathering cycle parameters for composites. The composites were exposed to either UV radiation and water spray or exposed to UV radiation only.*

Phase	Weathering cycle	Radiant exposure	Water spray exposure		Weathering time
			No. of cycles	Hours	
		$(J/m^2)^a$			(hr)
1	UV + water	42	500	100	1,000
		81	1,000	200	2,000
		122	1,500	300	3,000
	UV only	41	--	--	1,027
		81	--	--	1,991
		123	--	--	2,985
2	UV + water	66	800	160	1,600

[a] The irradiance at 300 to 400 nm integrated over time.

bulb changed periodically in order to maintain a constant irradiance. Radiant exposure, or amount of light energy, samples were subjected to was then determined (irradiance integrated over time). To allow for comparison between weathering cycles, radiant exposure, water spray exposure in terms of number of cycles and total time, and weathering time were recorded (Table 1).

Water soak

Two water soak procedures were followed in the second phase. The first procedure included drying composites in an oven at 105°C for 16 hours before soaking composites in a room temperature water bath for 160 hours. In the remainder of this paper, this is referred to as a single soak. Composites were also exposed to a cyclical soak. After oven-drying at 105°C for 16 hours, composites were exposed to a room temperature water bath for 8 hours. They were removed from the water bath, redried for 16 hours, and then soaked again for a total of 20 soaking-drying cycles. The total water exposure during the cyclical soak was also 160 hours. The composites were weighed after each soaking and drying period.

Color measurement

A Minolta CR-200 Chroma Meter (Minolta Corporation, Ramsey, NJ, USA) was used to measure color using the CIELAB color system. Lightness (L) was measured for five replicate samples. In the CIELAB color system, the value L can be thought of as a lightness fattor. L represents reflectance of a sample. An L of 0 means the sample does not reflect light; an L of 100 means the sample reflects 100 Percent light· An increase in L means the sample has faded or “lightened” (+ ΔL = lightening; $-\Delta$L = darkening).

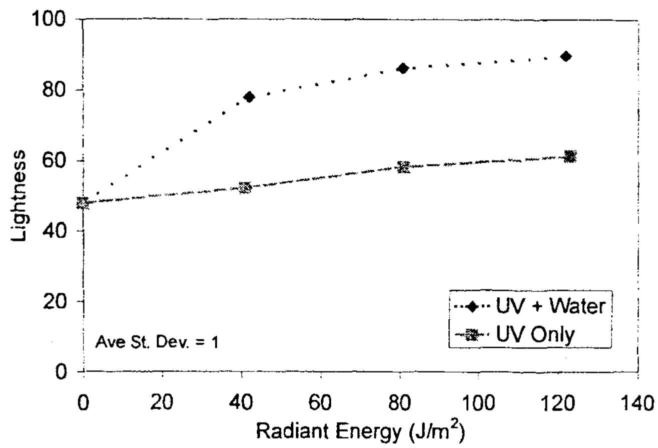

Figure 1. ~ *Average lightness of50% woodflour-filled HDPE composites during exposure to UV radiation with water spray or UV radiation only.*

Stastistics

To determine the significance of differences between unexposed and exposed composite properties, an analysis of variance (ANOVA) was carried out at a = 0.05. This was accomplished using Design Expert 6.0.0 software by Stat-Ease, Inc. (Minneapolis, MN, USA).

Results and Discussion

The effect of exposure to UV radiation with and without water spray on composite lightness is shown in **Figure 1.** All composites lightened during exposure; however, the change in lightness was much less when composites were exposed to UV radiation only, compared with exposure to UV radiation and water spray.

Composites consisting of 0, 10,20,30,40,50, and 60 percent wood flour content were exposed to a single soaking time period or in a cyclical series of 8-hour soaking periods and 16-hour drying periods. In each

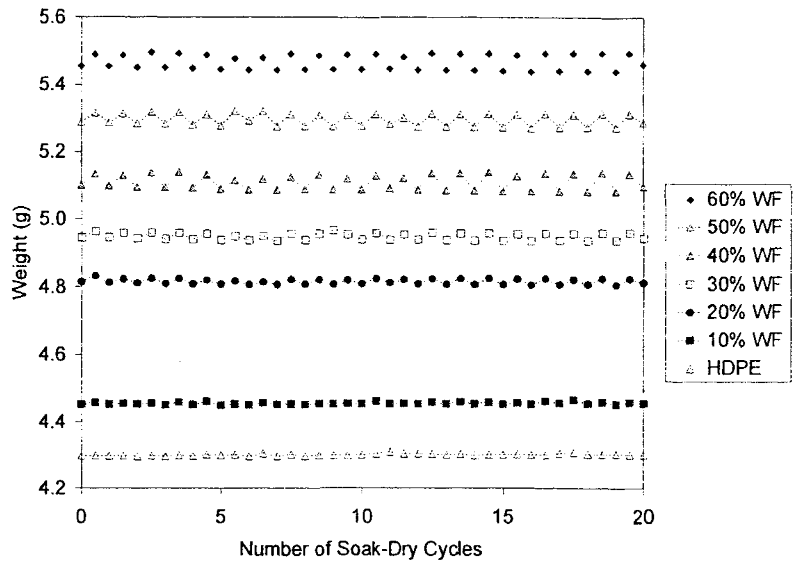

Figure 2. ~ *Weight of woodflour-filled HDPE composites after cyclical soaking and drying periods. Each series represents a single sample at its respective wood content.*

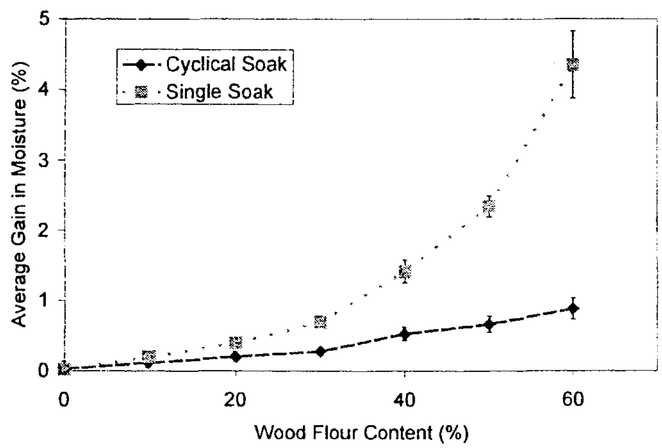

Figure 3. ~ *Average percent increase in moisture vs. wood flour content for composites exposed to a single water soak and a cyclical water soak, with a total of 160 hours of water exposure. Error bars represent one standard deviation.*

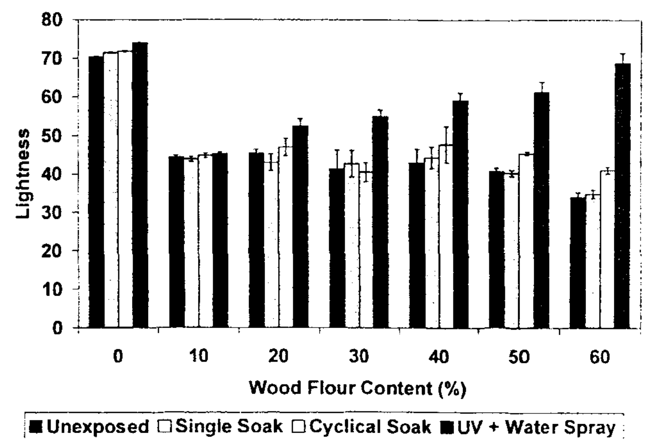

Figure 4. ~ *Average lightness of woodflour-filled HDPE composites VS. wood flour content. Average lightness is shown initially, and after exposure to a single water soak, a cyclical watersoak, and water spray with W radiation. Error bars represent one standard deviation.*

case, the total soak time was 160 hours. This was compared with exposure to UV radiation with water spray where the total water spray time was 160 hours **(Table 1).** During cyclical exposure, composites increased in weight after soaking and returned to their original weight after drying **(Fig. 2).** There was no apparent increase in weight per 8-hour soak as cycle number increased. **Figure 3** shows average moisture gain during each soaking period of the cyclical soak compared with average moisture gain after the single soak. Clearly, composites with more wood flour content had larger moisture gains after both the single soak and cyclical soak. In addition, composites exposed to the single soak experienced larger gains in moisture than those exposed to the cyclical soak.

The lightness of composites versus wood flour content, subjected to each of the exposures is shown in **Figure 4.** The lightness of composites exposed to the 160 hour single soak did not change much from the lightness of the unexposed composites. When composites were exposed to the cyclical soak for a total of 160 hours of water exposure, lightness increased slightly at higher wood flour contents. When composites were subjected to a weathering cycle that corresponded with 160 hours of total water exposure with W radiation composites lightened the most. The percent change in lightness after exposure can be seen in Table 2. The unfilled HDPE experienced slight increases in lightness for each exposure. There was no significant increase in lightness for any of the composites exposed to the single water soak, or for composites with 10 to 40 percent wood content exposed to the cyclical water soak. All composites exposed to UV radiation

Table 2. ~ *Percent change in lightness for composites exposed to 160 hours of water as a single soak, cyclical soak, or weathering cycle of UV radiation with water spray.*

Wood flour content	Single soak	Cyclical soak	UV +water spray
(%)			
0	2	2	5
10	ns[a]	ns	2
20	ns	ns	16
30	ns	ns	33
40	ns	ns	38
50	ns	12	51
60	ns	20	102

[a] ns = no significant change from the unexposed values at a = 0.05.

with water spray experience increases in lightness, and those with higher wood contents had larger increases in lightness.

In the first phase of this study, exposures were conducted so that radiant exposure and time were uniform, only water spray exposure varied. In the second phase, exposures were conducted so that total time of water exposure was consistent. Although direct comparison of lightness after exposure to UV radiation with water spray between phases 1 and 2 of this study is not possible because exposure time, radiant energy exposure, and water spray exposure are all different **(Table 1),** comparison between exposures within each of the phases is possible.

It is apparent that exposing WPCs to a combination of UV radiation and water spray is much more detrimental than exposing them to only W radiation, or only to water. The lightness of 50 percent woodflour-filled HDPE composites increased 87 percent when exposed to UV radiation with water spray, but only increased 28 percent when exposed to UV radiation only. Exposing 50 percent woodflour-filled HDPE composites to a single water soak resulted in no significant change in lightness; exposure to cyclical soaks resulted in a 12-percent increase in lightness; and exposure to water spray with W radiation resulted in a 51-percent increase in lightness (Table 2).

It was expected that composites with more wood flour content would have larger gains in moisture during exposure to both the single soak and cyclical soak. Because moisture absorption by the WPC is dependent on a diffusion rate, it was expected that composites exposed to 160 hours in a single soak would absorb more moisture than composites exposed to 20 cycles of 8 hours of soaking time followed by 16 hours of drying time. During exposure to UV radiation with water spray, exposure consisted of 12 minutes of water spray with UV radiation followed by 108 minutes of W radiation. During this time the environment changed between 35°C and 100 percent relative humidity (RH) during UV radiation and water spray exposure and 40°C and 30 percent RH during UV radiation exposure. Previously, 40 percent woodflour-filled PP composites exposed to an environment of 27°C and 30 percent RH for 2,000 hours absorbed approximately 0.5 percent moisture (9). This suggests that the moisture absorbed during exposure to UV with water spray was small. Although is it unlikely that there are large increases in moisture content of composites exposed to UV radiation with water, the water spray time of 12 minutes is clearly enough time to negatively influence lightness of the composites exposed in combination with UV radiation.

WPC color is primarily reflective of the color of the wood component. In virgin wood, the majority of colored substances are extractives (7). Exposing wood to UV light degrades primarily the lignin component, leaving cellulose at the surface, which can physically block UV light penetration. Similar to the mechanism that occurs when weathering wood, the water spray cycle can accelerate the rate of discoloration of WPCs through physical mechanisms. Washing the degraded surface by water spray exposes new wood surfaces for further degradation (10). Therefore weathering WPCs results in a cyclical erosion of the surface as lignin is degraded and subsequently washed away, exposing more lignin to degradation. Additionally, washing the surface can remove some water soluble wood extractives. Removal of the extractives, the main component that imparts color, is likely primarily responsible for the majority of color fade.

The increase in amount of hydrophilic cellulose at the wood surface and degradation of the more hydrophobic lignin has been shown to increase surface wettability (6). This may cause the composite surface to more readily absorb moisture. This is detrimental for two reasons. The first is that the presence of water in wood accelerates oxidation reactions that are a direct result of photodegradation. The second is that wood cell walls swell when penetrated by water. This facilitates light penetration into wood providing sites for further degradation (7) and creates microcracks in the composite, thereby accelerating degradation effects. All of these factors support the data, demonstrating that both UV radiation and water exposure are necessary for the dramatic lightening of WPCs.

Conclusions

Conducting weathering tests in the method described, recording radiant energy calculated at specific wavelengths, water spray exposure in terms of number of cycles and total time, and time of the weathering exposure, provides more insight into the weathering period. This not only allows for appropriate comparison between weathering cycles, but allows for the study of each weathering variable individually.

When this method is followed to compare the lightness of WPCs after exposure to UV radiation only, or exposure to water only, or both, dramatic differences can be seen. It becomes readily apparent that exposure to UV radiation with water spray resultsin significantly more lightening than exposure to either UV radiation only or water only. This suggests that the two weathering variables exhibit a synergistic effect which is detrimental to WPCs.

Acknowledgment

The author gratefully acknowledges the donation of wood flour from American Wood Fibers.

Literature Cited

1. Clemons, C. 2002. Wood-plastic composites in the United States: The interfacing of two industries. Forest Prod. J. 52(6):10-18.
2. Lundin, T. 2001. Effect of Accelerated weathering on the physical and mechanical properties of natural-fiber thermoplastic composites. MS thesis. Univ. of Wisconsin, Madison, WI.
3. Stark, N.M. and L.M. Matuana. 2003. Ultraviolet weathering of HDPE/wood flour composites. J. Appl. Polymer Sci. 90(10):2609-2617.
4. Stark, N.M., L.M. Matuana, and C.M. Clemons. 2004. Effect of processing method on surface and weathering characteristics of wood-flour/HDPE composites. J. Appl. Polymer Sci. 93(3):1021-1030.
5. Wypych, G. 1995. Handbook of Material Weathering. ChemTec Publishing, Toronto, ON, Canada.
6. Kalnins, M.A. and W.C. Feist. 1993. Increase in wettability of wood with weathering. Forest Prod. J. 43(2):55-57.
7. Hon, D.N.S. 2001. Wood and Cellulose Chemistry. Marcel Dekker, New York.
8. Hon, D.N.S. 2003. Weathering Testing Guidebook. Atlas Material Testing Solutions. Pub. No. 2062/098/200/AA/09/03.
9. Stark, N.M. 2001. Influence of moisture absorption on mechanical properties of woodflour-polypropylene composites. J. of Thermoplastic Composites. 14(5):421-432.
10. Williams, R.S., M.T. Knaebe, and W.C. Feist. 2001. Erosion rates of wood during natural weathering. Part II. Earlywood and latewood erosion rates. Wood and Fiber Sci. 33(1):43-49.

8th International Conference on Woodfiber-Plastic Composites (and other natural fibers)

May 23–25, 2005
Monona Terrace Community & Convention Center
Madison, Wisconsin, USA

Sponsored by the USDA Forest Service, Forest Products Laboratory
in cooperation with the American Institute of Chemical Engineers,
the Norwegian University of Science and Technology,
the University of Tennessee in conjunction with Oak Ridge National Laboratory,
the University of Toronto and Materials & Manufacturing Ontario,
and the Forest Products Society.

Forest Products Society
2801 Marshall Court
Madison, WI 53705-2295
phone: 608-231-1361
fax: 608-231-2152
www.forestprod.org