Changes in Wood Flour/HDPE Composites After Accelerated Weathering With and Without Water Spray

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Abstract

Wood–plastic lumber is promoted as a low-maintenance high-durability product. After weathering, however, wood–plastic composites (WPCs) often fade and lose mechanical properties. In the first part of this study, 50% wood-flour-filled high-density polyethylene (HDPE) composite samples were injection molded or extruded. 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 UV light compared with exposure to UV light and water spray. The change in modulus of elasticity (MOE) and strength was also much less when the composites were exposed to UV light only. The second part of the study involved stabilizing the WPCs with an ultraviolet absorber and or pigment. The stabilized composites were also exposed to the two weathering cycles. Again the amount of lightening and loss in mechanical properties was less when the composites were exposed to UV light only compared with exposure to UV light and water spray. The pigment was more effective than the ultraviolet absorber retaining composite properties. The pigment had a larger impact on property retention when the composites were exposed to UV light and 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. This is likely a result of the 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 the wood particles.

Introduction

Wood-derived fillers have recently made inroads into the thermoplastic industry, primarily as wood–plastic composites (WPCs) become more prevalent in the construction

industry. 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 being promoted as a low-maintenance high-durability product (1). However, the use of WPCs by the construction industry has resulted in concern about the durability of these products after weathering. Several papers report the weathering characteristics of polyethylene based WPCs. When exposed to accelerated weathering, WPCs often fade (2-5) and lose mechanical properties (2-4).

In current literature, a change in properties of WPCs after accelerated weathering is often reported after a given exposure time (2-5). However, during accelerated weathering measured variables can include exposure time, ultraviolet (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 severity 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 (6). In current WPC weathering literature, the radiant exposure is not known, and the amount of water exposure may not be reported, therefore comparisons between studies are often not possible.

There are many competing degradation mechanisms that occur while weathering WCs. UV exposure can result in changes in the polymer matrix as well as changes in the wood component. UV degradation of polyethylene 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 (7). Chain scission can result in more chain mobility and secondary recrystallization. Wood also undergoes photodegradation. The lignin at the surface of wood is primarily degraded, leaving a cellulose rich surface.

Wood is a naturally hydrophilic material, and water can be detrimental to its properties. As wood undergoes photodegradation, the cellulose rich surface increases the wettability even further, exacerbating the problem (8). Wood cell walls swell when penetrated by water, facilitating light penetration further into the wood providing sites for further degradation (9). Furthermore, washing the degraded surface with water exposes new wood surfaces for

degradation. Therefore weathering wood results in a cyclical erosion of the surface as the lignin is degraded and subsequently washed away, exposing more lignin to degradation. Washing can also remove some water soluble extractives that impart color to wood.

The weathering performance of WPCs can be influenced by the composite manufacturing method and the use of photostabilizers (3,4,10). The manufacturing method changes the WPC surface characteristics. Both processing methods and/or processing variables greatly influence the composite morphology and physical properties. This has been shown to change the moisture absorption characteristics (10) and weathering performance (4).

In order to protect against loss in color and mechanical properties, photostabilizers are often used in WPCs. Ultraviolet absorbers and pigments have been used to successfully decrease the percent loss in color and mechanical properties of WPCs after accelerated weathering (3).

Research to examine the relative importance of the water spray cycle during accelerated weathering has not been conducted. The main objective of our study was to understand how exposing WPCs with (a) different surface characteristics and (b) added photostabilizers to weathering cycles without and with water spray influence composite performance.

Experimental Methods

This study consists of two phases. In the first phase, unstabilized WPCs were manufactured via extrusion and injection molding. In the second phase, injection molded WPCs were protected with an ultraviolet absorber, pigment, or a combination of the two. During each phase the WPCs were analyzed after exposure to UV light only or to UV light and water spray.

Materials

The materials used in the first phase were wood flour (WF) and high-density polyethylene (HDPE). The WF 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 min and density of 0.963 g/cm^3 (Fortiflex A60-70-162, Solvay Polymers, Inc., Houston, TX, USA). A lubricant was added to aid in extrusion (Struktol TR016, density = 0.98 s/cm^3, Stow, OH, USA).

In the second phase, two photostabilizers were added to the WF/HDPE composites. A hydroxyphenyl benzotriazole ultraviolet absorber (UVA, Ciba Specialty Chemicals, Tinuvin 328, Tarrytown, NY, USA), and zinc ferrite pigment in a carrier wax (P, Cedar TI-8536, Holland

Colors, Richmond, IN, USA) were added to the composites. The WF was maintained at 50% by weight of the composite. The photostabilizers were included either independently or in combination with each other; the UVA added at 1 % and the P added at 2%. HDPE made up the remainder of the composite formulation.

Processing

Injection Molded–WF was dried for 24 h at 105°C. HDPE, WF, and photostabilizers if used, were then dry-blended manually at 50% WF until the mixture was well-mixed. Compounding was accomplished using a 32-mm Davis Standard (Pawcatuck, CT, USA) twin-screw extruder to produce homogeneous WF/HDPE composite pellets. The melt temperature at the die was 200°C and the melt pressure was 2.96 MPa. The pellets were dried at 105°C for at least 24 h prior to injection molding into flexural bar test samples. The composites were injection molded using a 33-ton Cincinnati Milacron (Batavia, OH, USA) injection molder. The mold nozzle temperature was 204°C, and the injection pressure reached a peak of 12.4 MPa. The American Society for Testing and Materials mold cavity used for the flexural samples was 120 by 3 by 12 mm (ASTM D790, 11).

Extruded–Extruded samples were manufactured at the University of Maine Advanced Engineered Wood Composite Center. The composite was 49% by weight WF, 8% by weight lubricant, and the remainder HDPE. A Davis Standard 94-mm twin-screw extruder was used with a die that produced a 30- by 140-mm radius edge profile. The die temperature was 180°C, and the die pressure was 2.1 MPa. Flexural samples (120 by 3 by 12 mm) were cut from deck boards for testing. The extruded surface was left intact.

Testing

Weathering – Composite samples were placed in a xenon arc-type light exposure apparatus and were exposed to *UV* light only or UV light and water spray. Samples were mounted on a drum that rotated around the xenon arc bulb at 1 rpm. For samples exposed to UV light only, the UV light exposure was continuous throughout the duration of weathering. If the water spray cycle was used, a 2-h cycle consisting of 108 min UV light exposure and 12 min simultaneous water spray and UV light exposure was followed. In both cases, an irradiance sensor was used to measure light intensity for wavelengths from 300 to 400 nm, the wavelengths that the majority of photodegradation occurs (XenoCal, Atlas Materials Testing Technology,

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

Table 1. Weathering cycle parameters for composites that were manufactured via either injection molding or extrusion (phase 1) and injection molded composites with photostabilizers added (phase 2). The composites were exposed to two different weathering cycles, exposure to UV only or UV with water spray.

Phase	Weathering Cycle	Radiant Exposure (J/m^2)[a]	Number of Water Spray Cycles	Time (h)
1	UV only	123	---	2985
1	UV + water	122	1500	3000
2	UV only	165	---	2985
2	UV + water	163	1500	3000

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

Color Measurement –A Minolta CR-200 Chroma Meter (Minolta Corporation, Ramsey, NJ) 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 factor. 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% light. An increase in L means the sample has faded or "lightened" ($+\Delta L$ = lightening; $-\Delta L$ = darkening).

Mechanical Properties –Composite samples can take a long time to reach equilibrium under traditional conditioning methods, therefore samples were oven dried at 105°C for 24 h before testing, to ensure the same conditioning for samples before and after weathering. Flexural tests were carried out according to ASTM D 790 (11) on a MTS 810 Material Test System (MTS Systems Corp., Eden Prairie, Minnesota). A 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. Five replicate specimens were tested for each formulation. The MOE and maximum strength were calculated according to the standard.

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

Results and Discussion

injection Molded versus Extruded Composites – Phase 1

The total change in lightness and flexural properties of injection molded and extruded composites after the two weathering cycles is summarized in Table 2.

Table 2. Percent change in property of injection molded or extruded WF/HDPE composites after exposure to either UV light only or UV light and water spray.

	Δ Lightness (%)		Δ MOE (%)		Δ Strength (%)	
	UV only	UV + water	UV only	UV + water	UV only	UV + water
Molded	28	87	22	-41	-10	-32
Extruded	13	46	-12	-52	1^{NS}	-34

^{NS}Difference between the unexposed and exposed mean is not significant at $\alpha = 0.05$

Lightness –The effect of both UV exposure and UV exposure with water spray on composite lightness is shown in Figure 1. The unexposed injection molded samples were darker than the extruded samples due to the higher processing temperatures. Both the injection molded and extruded composites lightened after each exposure. The change in lightness was much less when the samples were exposed to UV light only, compared with exposure to UV light and water spray. The lightness of the injection molded composites increased 87% when exposed to UV light and water, but only increased 28% when exposed to UV light only (Table 2). Similar trends were found for the extruded composites; the lightness increased 46% or 13%, respectively, when the composites were exposed to UV light and water spray or UV light only. This suggests that water spray has a large effect on composite fading.

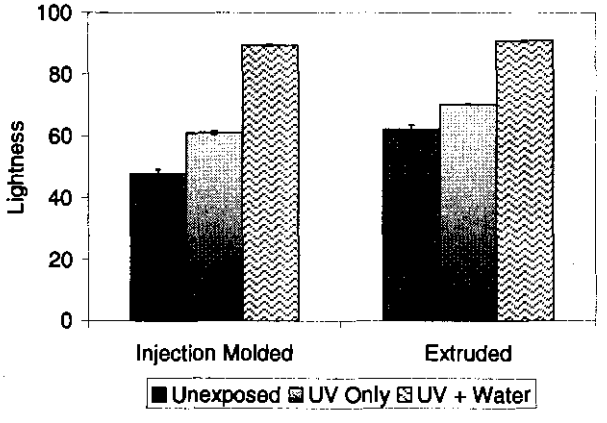

Figure 1. Change in composite lightness during exposure to UV light or UV light and water spray.

After exposure to UV light and water spray, both the injection molded composites and extruded composites lightened to similar values. WPCs color is primarily reflective of the color of the wood component. In virgin wood, the majority of colored substances are extractives (12).

Exposing wood to UV light degrades primarily the lignin component, leaving the cellulose at the surface, which can physically block UV light penetration. The water spray cycle can accelerate the rate of discoloration of wood through physical mechanisms. Washing the degraded surface by water spray exposes new wood surfaces for further degradation. Therefore weathering wood results in a cyclical erosion of the surface as the 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. Because composites manufactured via injection molding or extrusion had the same wood content, the composites lightened to similar values (Figure 1).

The increase in the amount of hydrophilic cellulose at the wood surface and the degradation of the more hydrophobic lignin has been shown to increase surface wettability (8). 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 the wood cell walls swell when penetrated by water. This facilitates light penetration into the wood providing sites for further degradation (9), thereby accelerating the degradation effects.

All of these factors support the data, demonstrating that water spray cycles are critical factors in the lightening of wood and correspondingly, the lightening of WPCs, particularly in combination with exposure to UV light.

Flexural Properties – Exposing the composites to UV light only resulted in an increase in MOE for the injection molded composites and a decrease in MOE for the extruded composites (Table 2). The increase in MOE of the injection molded composites (Figure 2) may be due to an increase in crystallinity of the polymer rich surface. It has been shown that during the initial stages of accelerated weathering, the crystallinity of the polymer surface of injection molded wood flour/HDPE composites increases (13). The HDPE matrix may also be crosslinking, this can occur during accelerated weathering UV exposure where temperatures are higher than natural weathering conditions (7).

Flexural MOE decreased when the composites were exposed to UV light and water spray (Figure 2). While the initial MOE values for the composites were similar, after weathering, the

MOE of the extruded composites decreased more than the MOE of the injection molded composites (Table 2).

The initial strength of the injection molded composites was higher due to the increased density of the composite and the resulting increase in efficiency of stress transfer from matrix to fiber (4). When exposed to UV light only, the strength of the injection molded composites decreased 10% while the strength of the extruded composites did not change significantly. Both composites exposed to UV light and water spray lost strength after weathering (Figure 3). A previous study reported that although the overall loss in strength was similar for injection molded and extruded composites, the larger losses in strength occurred earlier in the weathering period for the extruded composites compared with the injection molded composites. The composites with more wood at the surface, i.e. extruded composites, were more susceptible to strength loss after exposure to UV light and water spray due to the increase in pathways for moisture penetration (4).

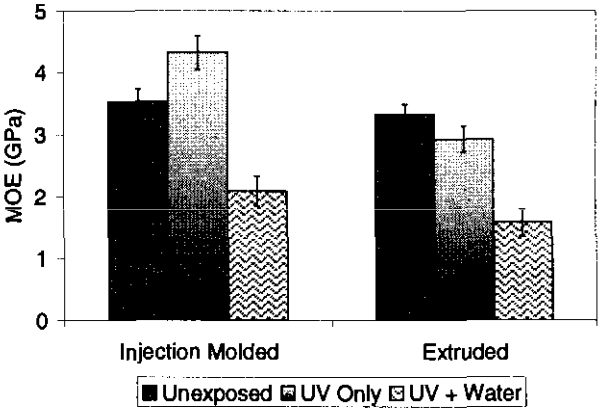

Figure 2. Change in composite MOE during exposure to W light or UV light and water spray.

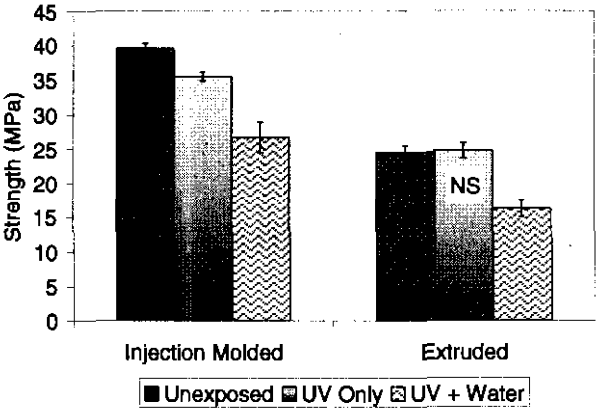

Figure 3. Change in composite strength during exposure to W light or UV light and water spray.

Moisture penetration into the WPC degrades the wood-polymer interface, which in turn causes loss of strength as the stress transfer from matrix to fiber becomes less efficient (14-16). For example, when injection molded HDPE composites filled with 40% wood fiber were exposed to a water bath for 2000 h, they experienced 22% decrease in flexural strength (14). Processing method has been shown to influence the amount of moisture the WPCs absorb, therefore influencing the amount of degradation of the wood-polymer interface. After soaking

50% WF/HDPE composites for 2 weeks, the more dense injection molded composites absorbed only 4% moisture while the less dense extruded composites absorbed 17% (10).

During accelerated weathering, the composites were not continuously exposed to water spray. However increased surface wettability as a result of UV light exposure and surface erosion, and the development of microcracks in the composite, likely allowed for increased moisture penetration as weathering continued. The water spray can erode the surface, making new composite surfaces available for water penetration and photodegradation. It was expected that the composites with more wood at the surface (i.e., the extruded composites) would be more susceptible to loss in strength after exposure to UV light and water spray.

Photostabilized Composites – Phase 2

The change in lightness and flexural properties after the two weathering cycle of injection molded composites with or without photostabilzers is summarized in Table 3.

Table 3. Percent change in properties of photostabilized WF/HDPE composites after exposure to either UV light only or UV light and water spray.

	Δ Lightness (%)		Δ MOE (%)		Δ Strength (%)	
Stabilizer	UV only	UV + water	UV only	UV + water	UV only	UV + water
---	43	115	25	-33	-2[NS]	-27
UVA	40	107	20	-21	5	-15
P	31	57	14	-18	2[NS]	-5
UVA + P	27	50	20	-16	5	–3[NS]

[NS]Difference between the unexposed and exposed mean is not significant at $\alpha = 0.05$

Lightness — Each of the composites in Phase 2 lightened upon weathering. Similar to the results from Phase 1, the composites generally lightened more when exposed to UV light and water spray compared with exposure to W light only. For each exposure, lightening decreased with the addition of each photostabilizer (Table 3). Although both UVA and P prevented some lightening after exposure to UV light and water spray, P was clearly more effective at preventing

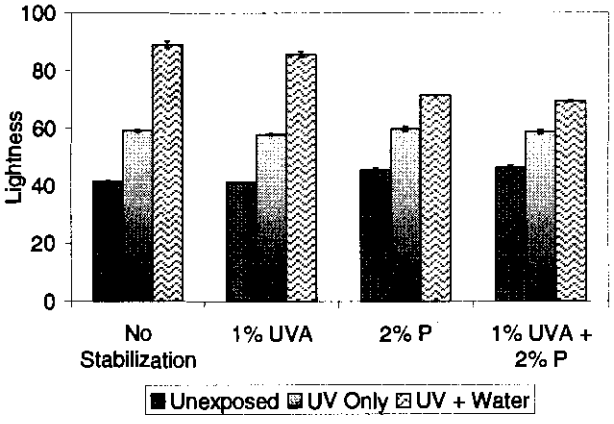

Figure 4. Composite lightness before exposure, and after exposure to UV light or UV light and water spray.

lightening. As Figure 4 illustrates, after exposure to UV light and water spray, the final lightness of the two composite formulations with P was lower than the others. After exposure to UV light only, the increase in lightness for the unstabilized composite was 43% (Table 3). The addition of UVA and P resulted in the increase in lightness of 40% and 31%, respectively. Similarly, after exposure to UV light and water, the increase in lightness for the unstabilized composite was 115%. The addition of UVA and P resulted in an increase in lightness of 105% and 57%, respectively. This clearly shows that UVA provides similar protection against lightening regardless of the exposure; however P is more effective at preventing lightening when composites are exposed to UV light and water spray. In this case, P is protecting against both UV exposure and moisture exposure. The addition of P blocks UV light, protecting the composite, and masked the wood bleaching. It may also be that the P, an inorganic pigment in a carrier wax, protected the wood particles from moisture penetration.

Flexural Properties – Figure 5 shows that exposure to UV light only resulted in an increase in MOE while exposure to UV light and water spray resulted in a decrease in MOE for all the composites in Phase 2. This was similar to the trend observed in Phase 1 for the injection molded composites. The increase in MOE after UV light exposure is likely due to a combination of increased crystallinity and cross-linking, both a result of UV degradation. Both the UVA and P protected against some photodegradation. The increase in MOE of the photostabilized composites was not as large compared with the unstabilized composites. After exposure

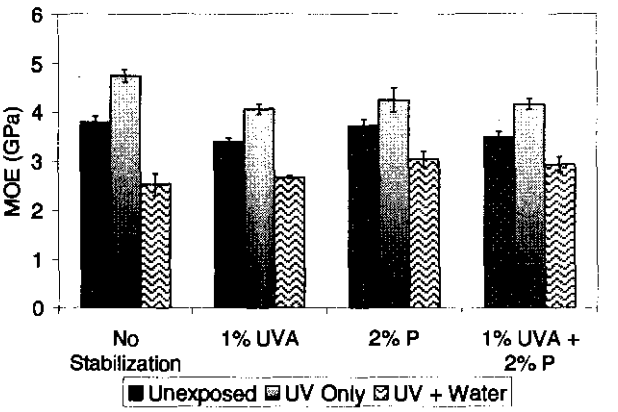

Figure 5. Composite flexural MOE before exposure, and after exposure to UV light or UV light and water spray.

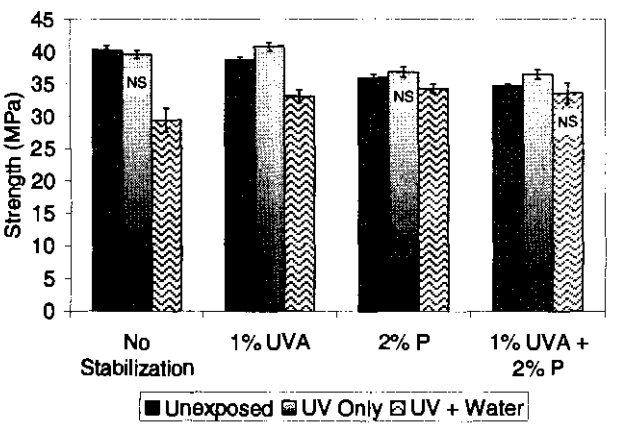

Figure 6. Composite flexural strength before exposure, and after exposure to UV light or UV light and water spray.

to UV light and water spray, the composites with UVA and P retained more MOE than the unstabilized composites (Table 3).

Figure 6 shows that the strength of the composites after exposure to only UV light was similar to the unexposed samples, and that the strength of the composites decreased or did not change after exposure to UV light and water spray. For each composite, the loss in strength after exposure to UV light and water spray decreased with the addition of UVA, P, or UVA + P (Table 3). The strength of the unstabilized composites decreased 27% after exposure to UV light and water spray. Adding UVA or P resulted in a loss in strength of 15% or 5%, respectively. This clearly shows that after exposure to UV light and water spray, the addition of both UVA and P resulted in smaller losses in strength compared with the unstabilized composites, and that P was more effective for strength retention than UVA. Adding both UVA and P together resulted in no statistically significant loss in strength. As with the protection against increase in lightness, it is likely that the carrier wax that is part of the pigment protected the wood particles resulting in some protection of the wood-plastic interface.

Conclusions

Exposure to both UV light and W light and water spray results in the lightening of WPCs. However, WPCs lighten more when exposed to UV light and water spray compared with exposure to UV light only. This is likely the result of the mechanical action of the water spray. The water spray removes the degraded layer, creating new surfaces available for degradation. The water spray also removes some color imparting water soluble extractives. Regardless of manufacturing method, the WPCs lighten to similar levels after exposure to W light and water spray (Figure 1). The addition of a pigment in a carrier wax can provide some protection against the deleterious effects of UV exposure and W exposure with water spray, resulting in less lightening. The addition of a pigment in a carrier wax is more beneficial when WPCs are exposed to both UV light and water spray compared with exposure to UV light only. It is likely that the pigment provides some protection against UV light exposure, while the carrier wax provides some protection against moisture exposure.

Exposure to W light results in an increase in flexural MOE if the composites have less wood at the surface, i.e., injection molded composites, and a decrease in flexural MOE for composites with more wood at the surface, i.e., extruded composites. All composites exposed to UV light and water spray decrease in flexural MOE. After exposure to UV light, the WPCs

generally experienced little or no change in strength. A decrease in strength was apparent after exposure to UV light and water spray. This indicates that water exposure is critical to the loss in mechanical properties of WPCs after weathering. The effects of water exposure can be slowed by manufacturing a composite with less wood component at the surface, such as would happen with injection molding versus extrusion. While both the ultraviolet absorber and pigment in a carrier wax were both effective in aiding mechanical property retention after exposure to UV light and water spray, the pigment is more effective in this manner, providing protection against both the negative effects of exposure to W light and moisture.

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