

# Effect of Durability Treatment on Ultraviolet Resistance, Strength, and Surface Wettability of Wood Plastic Composite

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A comparative analysis of photostabilizing effects of hindered amine light stabilizers (HALSs), an ultraviolet absorber (UVA), and zinc borate (ZnB) on wood plastic composites (WPCs) was made in this study to show the influence of the accelerated weathering on the surface degradation and loss of mechanical properties of treated WPCs. The results showed that the UVA was the most effective in preventing composite from being bleached, especially when the aging time was longer than 1000 hours. With the addition of the ultraviolet stabilizers, the contact angles increased, indicating increased water wettability. The contact angle of UVA-containing samples was greater than that of the control and the other samples treated with HALSs and ZnB. Flexural properties of all materials decreased after being weathered under xenon-arc light. Materials treated with UVA had higher retention rates in flexural strength and modulus. The results show that, among the agents used, UVA was the most effective additive in preventing WPCs from ultraviolet degradation.

*Keywords:* WPCs; Hindered amine light stabilizer; Ultraviolet absorber; Zinc borate; Surface degradation; Mechanical property

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## INTRODUCTION

As outdoor application of wood plastic composites (WPCs) is widespread, the durability of these products against weathering becomes a concern. It has been well documented that WPCs under accelerated weathering experienced color degradation, which affects their aesthetic appeal and mechanical performance (Lundin 2001; Stark and Matuana 2003). Exposure to ultraviolet (UV) radiation can result in property changes in both the polymer matrix and the wood components in WPCs. Wood undergoes photodegradation, and the degradation primarily occurs in lignin at the wood surface, leading to a cellulose-rich surface. As wood undergoes photodegradation, the cellulose-rich oxidized surface becomes more wettable. Photodegradation breaks molecular bonds, then generates free radicals at the composites' surface layer. These free radicals are terminated via chain scission. Then shorter chains derive from the chain scission and they are prone to re-crystallization due to their high mobility (Stark and Matuana 2007a, b; Taib *et al.* 2010). Under high energy of UV light, short molecular lines are initiated and combined, which form longer molecular chains and result in a greater modulus of elasticity (MOE) (Kalnins and Feist 2002).

Significant effort has been devoted to the development of photo-stabilized WPCs (Muasher and Sain 2005). UV stabilizers, including hindered amine light stabilizers (HALS) and ultraviolet absorbers (UVA), are often added to WPC formulations to minimize the adverse effects of UV radiation on WPCs (Stark and Matuana 2003). In addition, zinc borate (ZnB), which has been used in WPCs to protect them from potential biological deterioration, is also effective in inhibiting photo-degradation (Gnatowski *et al.* 2004). The effect of ZnB on lightness of wood fiber (WF) filled high density polyethylene (HDPE) composites after accelerated weathering tests was investigated (Gnatowski *et al.* 2004). The results of the study showed that ZnB hindered the degradation of WF/HDPE composites after the accelerated weathering. While this study clearly showed the effectiveness of ZnB in preventing WPC surface degradation, its effect on mechanical property loss in WPCs was not determined.

Lundin (2001) investigated the effect of hindered amine light stabilizer (HALS) content on the lightness and mechanical property loss of WF/PE composites weathered for 1500 h. The author reported that the addition of HALS (0.25% and 0.5% by weight) to the composites did not affect color change caused by accelerated weathering. Weathering reduced stiffness of the composites by 26% and 30%, respectively. On the other hand, the addition of 0.5% HALS reduced loss in flexural strength by 3%, though its statistical significance was not reported (Lundin 2001). Stark and Matuana (2003) reported the effect of UVA on lightness and mechanical property loss of WF/HDPE composites. The results showed that the addition of UVA (0.5% and 1% by weight) to the composites can minimize the effect of UV radiation after 3000 hours exposure. However, the increasing concentration did not change the amount of lightening (Stark and Matuana 2007a). A full-factorial experimental design was previously employed to examine the effect of a HALS, a low molecular weight UVA, and a high molecular weight UVA on lightness and mechanical properties of WF/HDPE composite exposed for up to 500 hours of accelerated UV weathering (Lee 2009). Only low molecular UVA significantly reduced composite lightening and loss in mechanical properties. Hindered amine light stabilizers were found to be ineffective in protecting the composite against surface discoloration and flexural property loss.

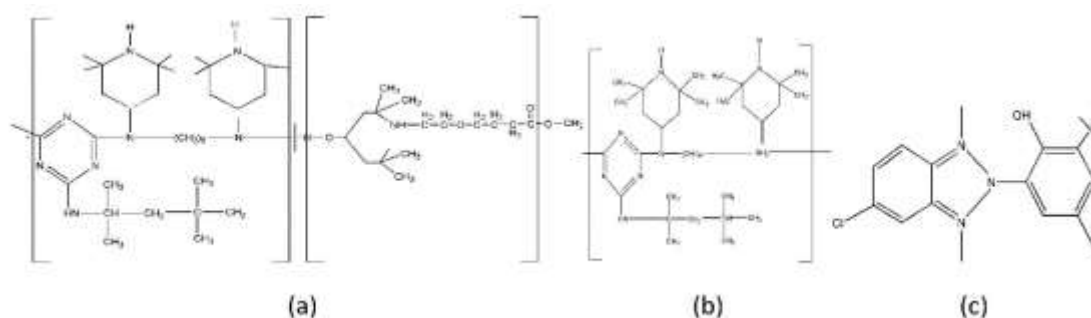
As far as we know, comparing the roles played by HALSs, UV absorbers, and ZnB in the UV degradation process for WPCs has rarely been reported. In this work, a comparative performance analysis of HALSs, UV absorber, and ZnB on the durability properties of HDPE-based WPCs were made. The objective was to study changes in surface morphology, color, water contact angles, and mechanical properties of the composites as influenced by various treatments.

## EXPERIMENTAL

### Materials

Pine wood flour (20 mesh particle size) was supplied by American Wood Fiber Inc. (Schofield, WI, USA). High density polyethylene (HD0760 with melt flow index, MFI=0.7 g/10 min at 190 °C/2.16 kg, density = 0.96 g/cm<sup>3</sup>) was provided by ExxonMobile Chemical Co. (Houston, TX, USA). Maleated polyethylene (MAPE) (Epolene™ G2608 with MFI = 6 to 10 g/10 min at 190 °C/2.16 kg, M<sub>w</sub>=65,000 g/mol) was utilized to increase the compatibility between fillers and the plastic matrix. Lubricant (TPW 306) provided by Struktol Co. (Stow, OH, USA) was used to improve the

processing of the WPC profile. Colorant was added to provide WPC with a wood-like appearance. UVA (Tinuvin 326) and HALS (Tinuvin 783 and Chimassorb 944) were chosen for this study. All of the HALS and UVA additives were supplied by Ciba Specialty Chemicals Inc. (Mississauga, Ontario). ZnB was purchased from the US Borax Co. (Greenwood Village, CO, USA). The chemical structures of the additives are shown in Fig. 1. All composite formulations are summarized in Table 1. The two HALS classes (Tinuvin 783 and Chimassorb 944) are based on antioxidants; and the UV absorber (Tinuvin 326) acts by absorbing UV radiation preferentially to polymers.



**Fig. 1.** Chemical structure of ultraviolet stabilizers used. (a) Tin783, (b) Chi944, and (c) UVA (Tin326)

**Table 1.** Formulation of Composites used in the Study

Sample code	Wood & Additive (wt %*)		HDPE (wt %)	HALS (wt %)		UVA (wt %)	ZB (wt %)
				Tin783	Chi944	Tin326	
Control.			31	NA	NA	NA	NA
HT-1				1			
HC-1	Wood	55			1		
AT-1	MAPE	2	30			1	
ZB-1	Lub	5					1
HT-2	Talc	5		2			
HC-2	Colorant	2			2		
AT-2			29			2	
ZB-2							2

Note: \*The content was based on the total composite weight. HT = Tinuvin 783; HC= Chimassorb 944; and AT= Tinuvin 326.

#### Composite manufacturing

The WF/HDPE/additive pellets were prepared using a Leistritz Micro-27 co-rotating parallel twin-screw extruder (Leistritz Corporation; Allendale, NJ, USA) with extrusion temperatures controlled at 155 (feeder), 160, 165, 170, 170, 170, 160, 150, 150, 150, and 155 °C (die) and the extruder rotation speed at 60 rpm. Profile extrusion was done using an Intelli-Torque Twin-Screw Extruder (CW Brabender Instruments; South Hanckensack, NJ, USA) and a 5 mm (thickness) x 50 mm (width) die. Manufacturing temperatures for the profile extrusion ranged from 150 (feeder), 165, 160, and 155 °C (die). The profile was air cooled and cut into various lengths for further testing.

Four groups of test samples with a size of 152x50x5 mm (eight from each formulation) were prepared. One group (four from each formulation) was used for

measuring initial bending modulus, strength and surface contact angle. The other three groups were used for the UV-exposure test.

## Methods

### *Accelerated UV weathering and color tests*

Accelerated artificial UV weathering tests were conducted in a Ci3000+ xenon arc-type weatherometer (Atlas Electric Devices; Wauconda) according to ASTM D2565-99 (2008) standard. The samples were rotated by the weatherometer at 1 rpm around a spray nozzle and a UV source. The weathering times were 500, 1000, and 2000 h.

Color change of the composites was measured using a Konica Minolta CR-10 spectrometer (Konica Minolta Corp.; Japan) with four replicates. At each interval, three points on each sample were tested and used to determine the color change. According to the CIELAB color system, color change ( $\Delta E_{ab}$ ) was calculated using the following equation,

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

where  $\Delta L^2$ ,  $\Delta a^2$ , and  $\Delta b^2$  are the differences between the final and initial values of lightness ( $L$ ) chromaticity coordinates ( $a$  and  $b$ ).

### *Surface contact angles*

The surface contact angles of unweathered and weathered samples were measured with a camera equipped with a goniometer eyepiece (Model JC2000C1, JinChen Corp.; China). The specimen was rested on a bracket attached to the stage, and then a small droplet of distilled water was placed on the specimen. The shape of each water droplet and sample surface at 24 °C were automatically captured and stored in a computer after measuring. The average of the contact angle for 12 droplets on each sample's surface was calculated and reported.

### *Mechanical property tests*

The flexural properties of the composites, including MOE and flexural modulus of rupture (MOR), were determined according to the ASTM D790-10 (2010) standard using an MTS Testing Machine. In brief, a three-point static bending test with a loading speed of 2.13 mm/min and a span of 80 mm was introduced. Four replicated specimens were tested for each treatment. The specimen size was 152x23x5 mm. The samples were conditioned at 20 °C and 65% relative humidity for 2 weeks before testing.

### *Scanning electron microscope and optical microscope measurements*

The morphology of the composites was measured using a XL30 environmental scanning electron microscope (SEM) (FEI; Hillsboro, OR, USA) with untreated and treated composite samples. The surfaces of the weathered samples were examined with a DE/AX10 optical microscope (Carl Zeiss; Germany).

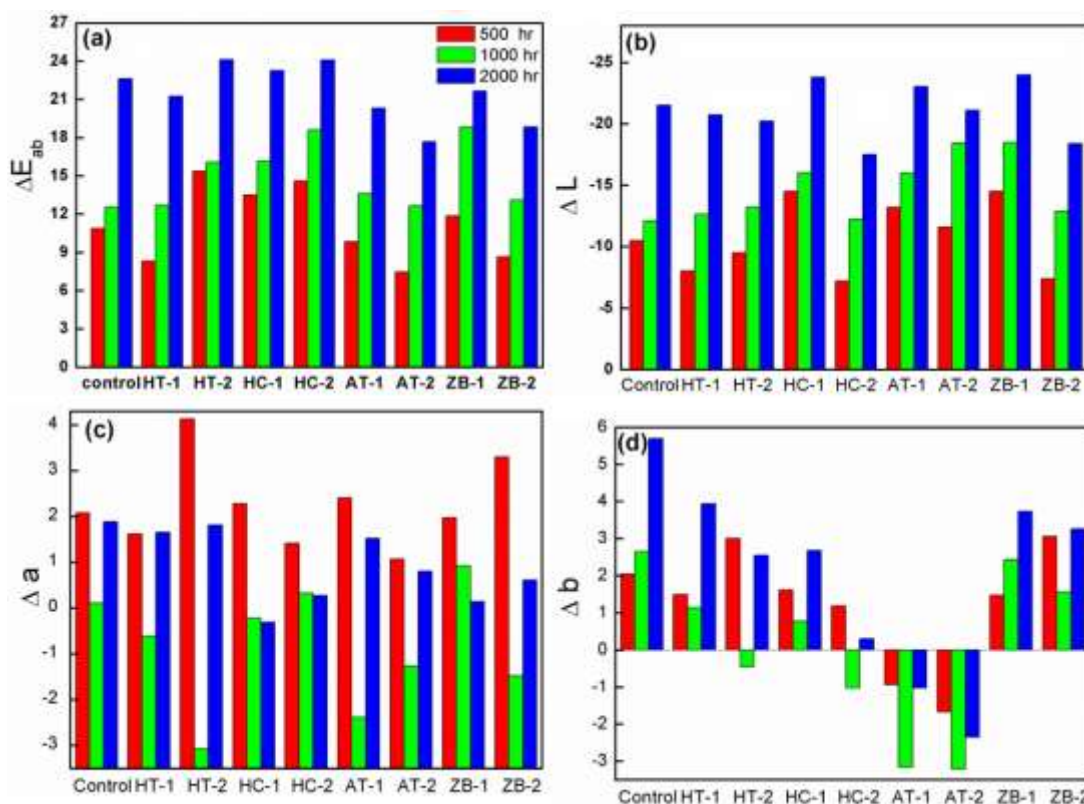
## RESULTS AND DISCUSSION

### Surface Degradation

#### Color difference

Measurement of discoloration was used to evaluate the photodegradation of the composites. As can be seen in Fig. 2a,  $\Delta E_{ab}$  values of all composites generally increased as the exposure time increased. Among the nine types of WPCs, HC-2 exhibited the highest  $\Delta E_{ab}$  after 2000 h of irradiation, which indicates the low stabilizing efficiency of HC. In comparison with HC, the WPCs/AT-2 exhibited the lowest  $\Delta E_{ab}$ . This feature suggested that UVA was more effective in improving the UV resistance. It should be pointed out that when the UV irradiation time was 500 h, HT-1 could also stabilize the composites as UV absorbers did. The order of the stabilizing effect exerted by different additives used was as follows (according to the value of  $\Delta E_{ab}$ ): UVA > ZB > HALS.

The  $\Delta L$  values for all composite formulations are presented in Fig. 2b. From this figure, it is clear that  $\Delta L$  values decreased as exposure time increased. The increasing trends indicated that UV irradiation exerted a discoloring effect. In addition, it was interesting to note that the decrease in  $\Delta L$  was very drastic during the first 500 h of irradiation, which shows that bleach was more obvious in the initial time. Compared with control, composites with 2% UV stabilizers exhibited the least  $\Delta L$  and addition of HC-2 revealed the least  $\Delta L$ . This indicated that the HC was better in regards to stabilizing the lightness of the composites than other types of additives did, and therefore resulted in better UV resistance.

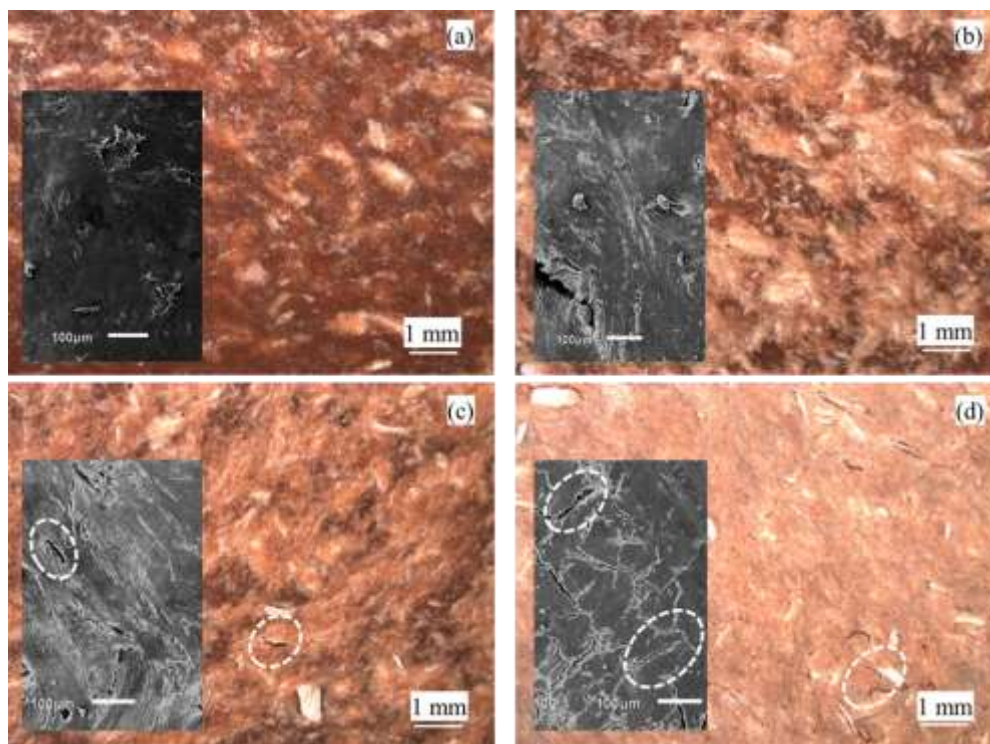


**Fig. 2.** Effect of exposure time and photo stabilizer type on (a)  $\Delta E_{ab}$ , (b)  $\Delta L$ , (c)  $\Delta a$ , and (d)  $\Delta b$  stabilized HDPE/WF composites

Figures 2c and 2d show  $\Delta a$  and  $\Delta b$  values of the composites. A decrease in “ $\Delta a$ ” indicates color change from red to green; while an increase in “ $\Delta b$ ” indicates the samples become more yellow. As shown, both “ $\Delta a$ ” and “ $\Delta b$ ” decreased with the increasing irradiation time for the control samples, indicating that the specimens became more green and yellow after UV irradiation. The decrease in “ $\Delta b$ ” was attributed to the oxidation of the lignin, which led to the formation of paraquinone chromosphere structures (Stark and Matuana 2003). These structures contributed to the yellow-color characteristic. With the incorporation of additives, it can be seen that the decrease in “ $\Delta a$ ” was lower compared with that of the control sample. For example, after 2000 hours of UV irradiation, AT-2 showed the lowest  $\Delta a$  (-0.6) compared with that of the control sample (-4.07). This result indicated that the UV absorber was the most effective one in preventing the decrease in “ $\Delta a$ ”. With regard to the “ $\Delta b$ ” value, it was interesting to note that although the HT-1, HT-2, ZB-1, and ZB-2 showed a decreasing trend like the control samples did, AT-1 and AT-2 exhibited the opposite trend. The  $\Delta b$  value slightly increased with the increasing irradiation time. This phenomenon revealed that UV absorbers generally helped composites avoid becoming more yellow, and indicated the stabilizing efficiency of UV absorbers.

### Surface morphology

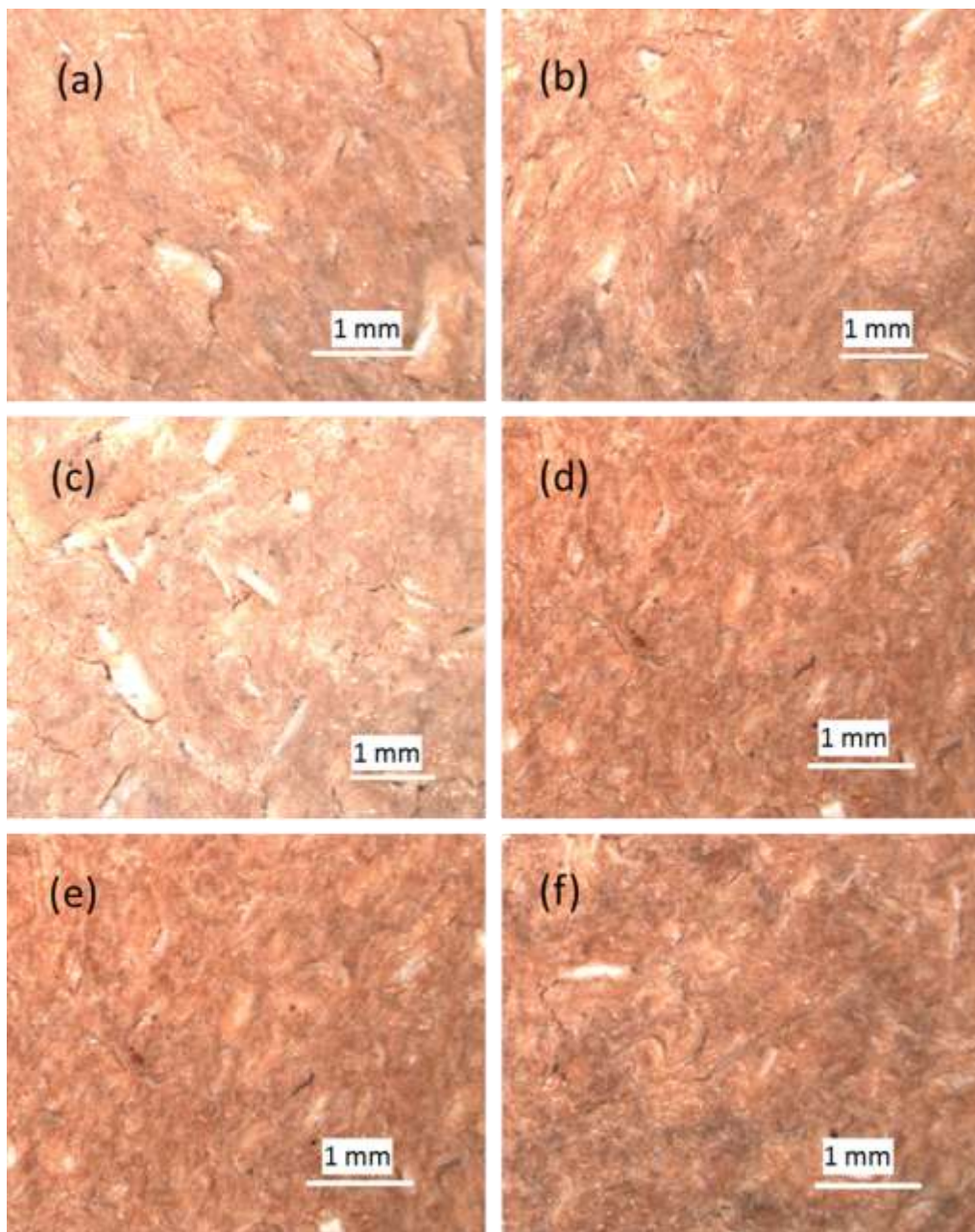
Ultraviolet irradiation usually influenced the surface morphology of samples. Optical micrographs of the surfaces of un-stabilized composites were taken at 0, 500, 1000, and 2000 h intervals of UV irradiation, and the data are shown in Fig. 3. As shown in the figure, when the irradiation time was 2000 h, the original dark brown surface became a white surface.



**Fig. 3.** Optical (background) and SEM (insert) micrographs of surfaces after UV exposure of (a) 0, (b) 500, (c) 1000, and (d) 2000 h



Such a change could be attributed to the breakdown of both lignocellulose materials and HDPE caused by UV irradiation. Therefore, the whiter the surface, the more serious UV degradation the sample suffered. In addition, with the increasing irradiation time, the surface became rougher and chalky. Surface cracks were also observed especially at longer exposure hours (SEM insets in Fig. 3), which were caused by the degradation of HDPE. All these results indicated the poor UV resistance of the control composites.



**Fig. 4.** Optical micrographs of WPCs after accelerated UV weathering for 2000 hours. (a) HT-1, (b) HT-2, (c) HC-1, (d) HC-2, (e) AT-1, and (f) AT-2

With the addition of additives, similar trends were observed when samples underwent harsh weathering, except for composites with the UV absorber. For example,

after 2000 h of irradiation, the surface morphology of AT-2 (*i.e.*, AT326-2) was not faded seriously (Fig. 4). There were fewer surface cracks, indicating the improved UV resistance provided by UVA. The results of surface morphology indicated that UVA was the most effective regarding to the improvement in UV resistance, which was consistent with results of color difference.

### Surface Wettability

Surface contact angle was measured to determine the influence of UV irradiation on the wettability of composites and measured values are listed in Table 2. It is evident from the tabulated data that addition of UV stabilizer increased the WPC's contact angle. Among the composites treated with UV stabilizers, WPCs/AT and WPCs/ZnB had larger contact angles, while HALSs had lower values. In general, the wettability of WPCs was determined not only by the surface hydrophilic wood fiber loading, but also by the interfacial adhesion of the composites (Lu and Wu 2005). According to this point, UVA samples had a better interfacial bonding than others. The contact angles of all WPCs ranged from 90° to 123°.

**Table 2.** Effects of UV-stabilizer on Surface Wettability of WPCs

Sample Code	Contact angles ( $\theta^\circ$ )				
	0 h	500 h	1000 h	2000 h	
control	93(6.1)	70.5(5.4)	67.3(3.5)	74.0(3.0)	
HT	1	95.4(4.9)	63.4(2.9)	71.8(2.7)	77.9(3.8)
	2	93.5(2.2)	67.6(4.5)	72.8(1.9)	78.6(2.8)
HC	1	93.5(1.3)	58.6(5.0)	70.6(2.7)	70.6(3.4)
	2	93.7 (1.1)	66.1(4.3)	73.2(2.4)	71.5(4.7)
AT	1	122.6 (4.5)	67.9(3.3)	82.2(1.0)	82.4(1.3)
	2	117.2 (2.5)	74.0(5.2)	82.1(2.0)	82.7(1.3)
ZB	1	103.7(3.4)	77.2(3.7)	76.2(3.5)	76.3(1.3)
	2	98.9(3.8)	76.4(3.5)	72.8(2.6)	75.6(4.2)

\* Mean values of each property; numbers in parenthesis are standard deviation based on four specimens

After weathering, the samples exhibited lowered contact angle values (*i.e.*, increased wettability) regardless of the type and amount of additives used. The order of the contact angle values was AT (82.4°) > HT (77.9°) > ZB (76.3°) > HC (70.6°) at 2000 hours. This order corresponds well with the results of the optical microscopy data. UVA composites showed the least number of cracks (Figs. 3 and 4), while the HC showed more cracks and verified the better stabilizing effect of UV absorbers. It should be pointed out that contact angles of composites that contain a UV stabilizer did not linearly decrease with the increasing irradiation time. The contact angle increased slightly from 500 hours to 1000 hs. This might be explained by the possibility that hydrophilic wood component of the WPCs was washed away as affected by the combined UV/water spraying treatment process and therefore increased the value of contact angle (Lundin 2001).



## Mechanical Properties

Table 3 summarizes the effect of accelerated weathering on the MOR and MOE. The flexural strength (MOR) of HDPE/WFs control was 32.5 MPa (Table 3). The control samples showed little strength loss after the weathering treatment, indicating that the greatest degree of weathering was experienced by the sample surface (Lee 2009). With the use of the additives, sample strength from all groups decreased. Since wood fiber content in all groups was the same, the data showed some negative effect of using the additives on composite strength - weakening interfacial bonding between wood fiber and plastic matrix under weathering conditions (Table 3). From Table 3, it is clear that MOR generally decreased as time increased. Among these composites, the UVA-treated WPCs retained the greatest MOR over the weathering period, while the HC-based WPCs retained the least. This result corresponded well with the aforementioned results of color difference, surface wettability, and optical micrographs. The HDPE underwent severe chain scission during UV weathering. Also, wood fibers swelled and shrank after absorbing and desorbing moisture, which left cracks and voids at the interface between the lignocellulosic material and polymer matrix. The stress could then not be transferred smoothly from matrix to fibers, which led to the strength loss.

**Table 3.** Strength of HDPE Composite with UV-stabilizer

Sample Code	MOR (MPa)	MOR retention ratio (%)			MOE (GPa)	MOE retention ratio (%)		
		500 h	1000 h	2000 h		500 h	1000 h	2000 h
Control	32.5*(0.57)	99	97	98	4.6(0.10)	98	100	89
HT	1 31.1(1.20)	91	94	79	4.3(0.06)	93	91	73
	2 28.5(0.65)	88	96	84	4.4(0.07)	90	96	80
HC	1 31.8(1.18)	92	90	76	4.5(0.11)	94	92	74
	2 29.5(1.56)	92	93	88	4.6(0.08)	94	92	78
AT	1 28.9(1.16)	86	96	81	4.2(0.22)	86	99	81
	2 30.7(1.58)	95	99	93	4.6(0.13)	97	99	92
ZB	1 28.8(0.99)	83	85	78	4.1(0.03)	86	84	74
	2 24.9(0.41)	78	80	75	3.7(0.06)	82	79	70

\* Mean values of each property; numbers in parenthesis are standard deviation based on four specimens

Similar to the trend observed for the MOR, MOE declined with addition of UV stabilizer. The control samples showed little modulus loss after the weathering treatment. The treated samples showed different levels of modulus reduction among difference groups. MOE retention ratios at the 1% additive adding level were in the order of AT (81%) > HT (74%) = ZB (74%) > HC (73%) after 2000 h of irradiation.

## CONCLUSIONS

1. All WPC materials underwent surface degradation when they were artificially weathered. Compared with HALS and ZnB, UVA was more effective in preventing composite lightening, especially when the aging time was longer than 1000 h.

2. Adding UV stabilizer generally gave rise to larger surface contact angles and composites, with UVA exhibiting the largest value. All contact angle values were decreased after exposure of artificial xenon light and water spray treatments. Ultraviolet absorber-based composites exhibited a better performance in preventing surface degradation at 2000 h.
3. The use of UV additives led to reduced flexural modulus and strength in the composite samples. After exposure to combined xenon-arc light and water spraying, all MOR and MOE values were decreased slightly. Among these materials, composites with UVA had the highest MOE and MOR values. In addition, they also showed the greatest retention rates in both MOR and MOE after weathering.

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## REFERENCES CITED

- ASTM D790-10 (2010). "Standard test methods for flexural properties of unreinforced and reinforced plastics and electrical insulating materials," *ASTM International*, West Conshohocken, PA.
- ASTM D2565-99 (2008). "Standard practice for xenon-arc exposure of plastics intended for outdoor applications," *ASTM International*, West Conshohocken, PA.
- Gnatowski, M., Mah, C., and Manning, M. (2004). "Evaluation of wood plastic composite photo-degradation using modern microscopic and spectroscopic methods," *IUPAC World Polymer Congress, MACRO 2004*, Paris, France, July 4-10.
- Kalnins, M. A., and Feist, W. C. (2002). "Increase in wettability of wood with weathering," *Forest Prod J.* 43(2), 55-57.
- Lee, S. Y. (2009). "Color change and tensile properties of wood flour reinforced polypropylene composites: Influence of photo-stabilizer," *Journal of the Korean Oil Chemists' Soc.* 26(2), 171-178.
- Lundin, T. (2001). "Effect of accelerated weathering on the physical and mechanical properties of natural-fiber thermoplastic composites," M.S. thesis, University of Wisconsin-Madison.
- Lu, J. Z., and Wu, Q. L. (2005). "Surface and interfacial characterization of wood-PVC composite: Imaging morphology and wetting behavior," *Wood and Fiber Science* 37(1), 95-111.
- Muasher, M., and Sain, M. (2005). "The efficacy of photostabilizers on the color change of wood filled plastic composites," *Polymer Degradation and Stability* 91(5), 1156-1165.
- Stark, N. M., and Matuana, L. M. (2003). "Ultraviolet weathering of photostabilizer wood-flour-filled high-density-polyethylene composites," *Journal of Applied Polymer Science* 90, 2609-2617.

- Stark, N. M., and Matuana, L. M. (2007a). "Characterization of weathered wood-plastic composite surfaces using FTIR spectroscopy, contact angle, and XPS," *Polymer Degradation and Stability* 92(10), 1883-1890.
- Stark, N.M., and Matuana, L. M. (2007b). "Influence of photostabilizers on wood flour-HDPE composites exposed to xenon-arc radiation with and without water spray," *Polymer Degradation and Stability* 91(12), 3048-3056.
- Taib, R. M., Zauzi, Ahmad, N. S., Ishak, Mohd, Z. A., and Rozman. H. D. (2010). "Effects of photo-stabilizers on the properties of recycled high-density polyethylene (HDPE) /wood flour (WF) composites exposed to natural weathering," *Malaysian Polymer Journal* 5(2), 193-203.

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