

# Color Change and Tensile Properties of Wood Flour Reinforced Polypropylene Composites; Influence of Photostabilizers

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**Abstract** : A comparative analysis of the hindered amine light stabilizers (HALS) and UV absorber (UVA) and their respective photostabilizing effect on wood plastic composites (WPCs) are reported in this study. The influence of accelerated weathering on the mechanical properties of the composites and the microscopic morphology of a degraded layer on the cross section and the surface were studied. UV absorbers were more efficient at preventing composite lightening than was UV stabilizer. The amount of whitening decreased with the increase of photostabilizers. With the addition of a UV absorber (Tinuvin360), the tensile modulus and strength of the composites increased slightly. However, the addition of a light stabilizer (Tinuvin770) and a UV absorber decreased the tensile modulus and strength of the composites. After 250 and 500 hr exposure, tensile modulus and strength of the unstabilized and stabilized composites decreased. The tensile strength of UV absorber (Chimassorb81)-stabilized composites was significantly greater than that of control and light stabilizer (Tinuvin770)- and UV absorber (Tinuvin360)-stabilized composites. UV absorber-stabilized samples showed less whitening and photodegradation than control and light stabilizer-stabilized samples.

*Keywords* : PP, wood flour, light stabilizer, UV absorber, weathering

## 1. Introduction

Wood Plastic Composites (WPCs) have been manufactured by incorporating particulate natural fillers into a polymer matrix to fit the various industries such as deck boards, railing, fencing, landscaping, window profile, marina, sound-proof wall and automobiles. In 2006, the market for WPC

industry was estimated at about 2.2 billion pounds and valued at over \$750 millions. The WPC market is expected to reach 3.6 billion pounds by 2009 [1,2]. WPCs are susceptible to color change and weathering resulting from ultraviolet (UV) radiation. Whereas the weatherability of a material is dependent upon its resistance to all weather elements, the radiation of the sun, particularly the UV portion is mainly responsible for limiting the lifetime of WPCs exposed to the environment [3]. The single most significant component of

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simulated weather is the nature of the radiation source.

Test devices with artificial light sources are generally used to accelerate the photodegradation because of the need for more rapid resistance to weathering than can be obtained by outdoor exposure tests and the need for controlled conditions. The light sources in the test devices include two types of filtered carbon arcs, filtered xenon arcs, and metal halide or fluorescent UV lamps. The xenon arc is strongly preferred as a light source when the material to be tested will be exposed to natural sunlight. Xenon has been extensively adopted by the automotives, polymer additive and textile industries in particular, and is generally replacing carbon arc technology [4].

UV radiation is extremely destructive to polymeric materials and the energy in UV radiation is strong enough to break molecular bonds of the materials [5]. This behavior in the polymeric materials brings about thermal oxidative degradation, which results in embrittlement, discoloration, or overall reduction in mechanical properties [6,7]. On the other hand, cellulose and lignin, two major components of wood often discolor when exposed to outside conditions.

UV stabilizers protect WPCs from UV radiation present in sunlight, which could degrade mechanical properties and cause color changes [8]. UV stabilizers are organic compounds which are radical scavengers or hydroxyperoxide decomposers, the most prominent of which are hindered amines, called hindered amine light stabilizers (HALS). These additives protect WPCs both during processing and for the service life of the product and their use has improved ageing process and appearance of most WPCs. The HALS have been used for protecting polyolefin as free radical scavengers [9]. It was reported that they photostabilize unfilled high density polyethylene (HDPE) and polypropylene (PP).

UV absorbers (UVA) are also used as photostabilizers in polyolefins such as HDPE and PP and their protection mechanism is based on the absorption of harmful UV radiation and its dissipation as heat [10]. However, the photodegradation mechanism of WPCs is complicated because each component, namely wood flour and polymer, may be degraded by means of a different mechanism. The mechanical properties of WPCs depend on the interaction and adhesion between the polymer matrix and the wood filler. Degradation of the interface caused by weathering may reduce the ability of the composite to effectively transfer stress between these components, resulting in lowered mechanical properties.

A comparative analysis of the HALS and UVA and their respective photostabilizing effect on WPCs has not been reported. The objective of the research was to evaluate the relative durability of photostabilizer-filled WPCs intended for decking applications, based on an accelerated weathering test. The influence of accelerated weathering on the mechanical properties of the composites and the microscopic morphology of a degraded layer on the cross section and of the composition were studied.

## 2. Experimental

### 2.1. Materials

Wood flours of 100-120 mesh (WF, Lignocel C120) were purchased from J.Rettenmaier & Sohne Co. (Rosenberg, Germany). Neat polypropylene (PP,  $M_w = 180,000$  g/mol, Korea Petrochemical Co., Korea) has a melt index of 3.2 g/10min and a density of 0.9 g/cm<sup>3</sup>. One HALS (Tinuvin 770) was chosen for this study. Also, two UVAs (Tinuvin 360 and Chimassorb 81) were chosen based on differences in molecular structure. Table 1 summarizes all the additives in this study and chemical structures are shown in Fig. 1.

Table 1. Photostabilizing additive description and formulation

Additives	Trade name	Molecular mass(g/mol)	Additive description
Light stabilizer	Tin360	659	UVA (benzotriazole)
	Tin770	481	HALS (low m.w. diester)
UV absorber	Chi81	326.4	UVA (benzohexone)

All of the HALS and UVA additives were Dogbone test specimens were molded in a

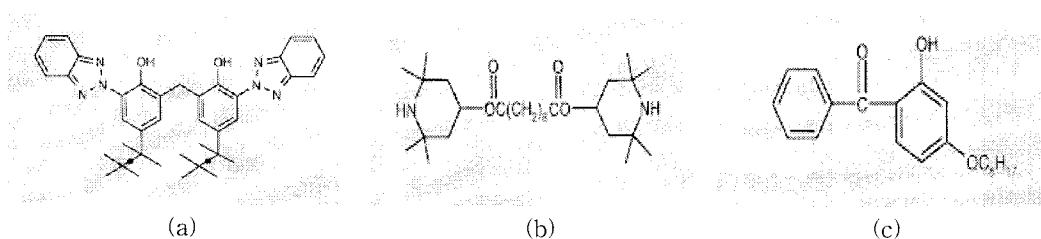


Fig. 1. Chemical structures of photostabilizers. a) Tin 360, b) Tin770, c) Chi81.

supplied by Ciba Specialty Chemicals (Mississauga, Ontario).

## 2.2. Melt compounding

The WF/PP blends were prepared with a co-rotating twin-screw extruder of a screw diameter of 19 mm with an L/D ratio of 40 (Bautek Co, Korea). A compounding temperature and screw speed were 180°C and 100-150 rpm, respectively. The compounding formulations were WF (fixed 50 wt%) and PP (50 wt% but arranged according to weight fraction of photostabilizers). HALS and UVA were added to the WF and PP mixture in 0.5, 1.0 and 2.0 wt%. The extrudate in the strand form was air-cooled and pelletized. The composite samples were dried at 80°C for 24 hr in a vacuum oven to remove the absorbed moisture before being injection molded at 190°C and then cooled to room temperature.

## 2.3. Tensile properties

The tensile test for composites was performed according to ASTM D638 using an Universal Testing Machine (Zwick Testing Machine Ltd., Leomister, United Kingdom).

size of 3.18 x 9.53 x 3.00 mm. Tensile strength and modulus were determined with an extensometer at a crosshead speed of 10 mm/min. Five replicated specimens were tested for each treatment.

## 2.4. Accelerated weathering

The composite samples were placed in a xenon arc-type light exposure apparatus operated according to ASTM D 2565. Test samples were rotated by the weatherometer at 1 rpm around a spray nozzle and UV source. The device was set to provide 102 min of light, followed by 18 min of light and water exposure, exposing one side of the specimens to direct light and water spray while subjecting both sides to high levels of humidity. To understand the initial effect of UV exposure, samples were removed for analysis after 250 and 500 hr exposure.

## 2.5. Optical properties

A spectrometer CM-3600D (Konica Minolta Sensing, Inc., Japan) was used to measure color of the weathered composites. Lightness ( $L^*$ ) and chromaticity coordinates ( $a^*$  and  $b^*$ ) were measured for five replicates, and color

change ( $\Delta E_{ab}$ ) was determined with the procedure outlined in ASTM D 2244:

$$\Delta E_{ab} = \text{SQRT}(\Delta L^2 + \Delta a^2 + \Delta b^2)$$

where  $\Delta L$ ,  $\Delta a$  and  $\Delta b$  represent the difference between initial and final values of  $L$ ,  $a$  and  $b$ , respectively. The value  $L$  is a lightness factor which an increase in  $L$  means the sample is lightening (i.e., a positive  $\Delta L$  for lightening and a negative  $\Delta L$  for darkening). A positive  $\Delta a$  indicates a color shift toward red, and a negative  $\Delta a$  indicates a color shift toward green. A positive  $\Delta b$  indicates a shift toward yellow, and a negative  $\Delta b$  indicates a shift toward blue.

## 2.6. Optical microscope

In order to obtain the transverse and vertical micrographs of the weathered samples, specimens were examined with an optical microscope (DE/AX10, Carl Zeiss, Germany).

## 3. Results and discussion

### 3.1. Color change after UV exposure

Composite samples were exposed to UV radiation and water spray for 250 and 500 hrs. Fig. 2(a) shows that for all composite formulations  $L^*$  increased, but the increase in  $L^*$  was not linearly related to exposure time. This increase is indicative of color fading of the weathered composites. The largest increase in  $L^*$  occurred after 250 hr exposure time. The difference in  $L^*$  between the formulations became pronounced as the exposure continued to 500 hr exposure time. The results clearly show that composites with UV absorbers and a light stabilizer did not lighten in color as much as the unstabilized composite. The samples with a light stabilizer lightened slightly less than did the unstabilized composite (PP50WF50). All

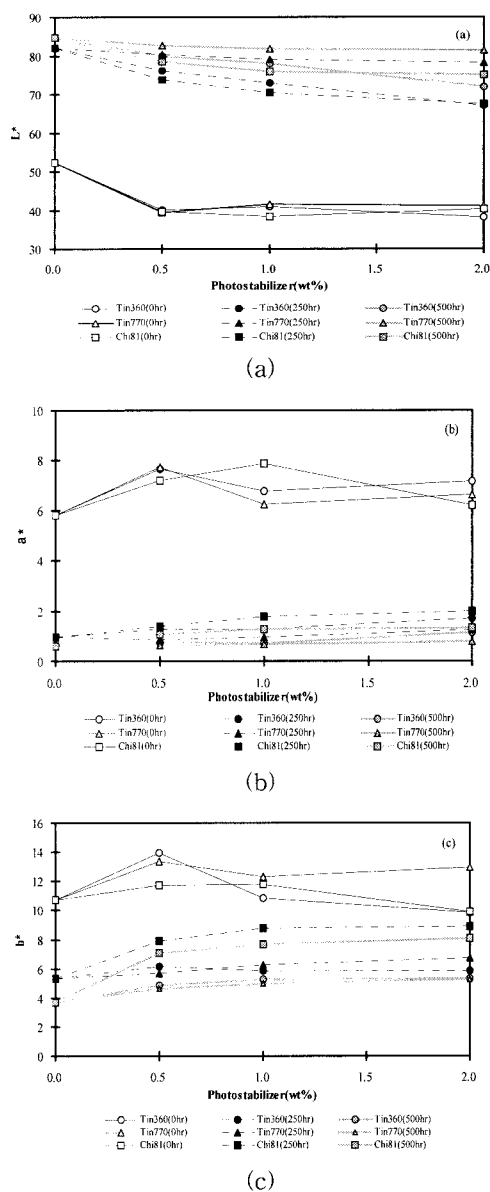


Fig. 2. Effect of exposure time and addition levels of photostabilizers on a) final lightness, b) color parameter  $a^*$  and c) color parameter  $b^*$  of photostabilized PP/WF composites.

composites with UV absorbers showed less lightening than the unstabilized composite. The addition of 0.5, 1.0, and 2.0% UV absorbers had a greater effect on  $L^*$  than did

the addition of 0.5, 1.0, and 2.0% light stabilizer. Therefore, UV absorbers were more efficient at preventing composite lightening than was UV stabilizer. The amount of lightening decreased with the increase of UV absorbers and UV stabilizer. These results may suggest that composite lightening may be due to bleaching of the wood component in the composites [8]. The UV absorbers reduce lightening by absorbing some UV radiation, resulting in less UV radiation available to bleach the wood component. The addition of UV absorbers to the composites absorbs some UV radiation before the wood is exposed and bleached [11].

Fig. 2(b) shows that the  $a^*$  value of the composites increases with the addition of a light stabilizer and UV absorbers, compared to the PP50WF50. But there is no significant relationship between the  $a^*$  and the loading level of photo-additives. An increase in  $a^*$  indicates color change from green toward red. The  $a^*$  value decreases significantly with exposure time for the control and for a light stabilizer- and UV absorber-stabilized samples in the first 250 hrs. The UV absorber (Chi81)-stabilized sample showed the highest  $a^*$  value, compared to the UV absorber (Tin360) and light stabilizer

(Tin770). As UV exposure time increased to 500 hrs, the  $a^*$  value of the composites decreased. On the other hand, the decrease in  $b^*$  indicates color change from yellow to blue. Since the  $b^*$  value represents the yellowing of the sample, it is speculated that the decrease in the  $b^*$  in 250 and 500 hr exposure is due to the oxidation of the lignin which leads to the formation of paraquinone chromophoric structures (Fig. 2(c)). These structures have a characteristic yellow color. However, since all the samples including the control experience the decrease in the  $b^*$  value after 250 hr exposure, it can be proposed that the chromophores undergo degradation which leads to photobleaching.

### 3.2. Tensile properties

Tensile modulus and strength values were calculated from the tensile test data (Table 2). The tensile modulus and strength of PP50WF as control were 97.7 and 27.3 MPa (Table 2). With the addition of a UV absorber (Tin360), the tensile modulus and strength of the composites increased slightly. This increase may be due to the increase in stiffness of the composites and internal bond strength between polypropylene and wood flour. However, the addition of a light stabilizer (Tin770) and a UV absorber

Table 2. Tensile properties after 250 and 500 hr exposure of WPCs

Formulation				Tensile modulus(MPa)			Tensile strength(MPa)		
PP (wt%)	WF (wt%)	Photostabilizers (wt%)		0hr	250hr	500hr	0hr	250hr	500hr
50	50	-	0	97.7(2.0)	90.7(1.7)	90.3(2.9)	27.3(0.5)	27.0(0.7)	26.3(0.2)
49.5	50	Tin360	0.5	100.2(0.7)	89.6(1.6)	90.5(0.9)	28.4(1.6)	26.8(0.2)	25.9(0.8)
49	50		1	98.2(4.1)	91.2(3.2)	89.3(1.8)	29.4(0.8)	27.8(0.3)	26.9(0.7)
48	50		2	98.4(2.9)	93.1(1.7)	91.5(3.5)	29.3(0.4)	28.4(0.7)	28.2(0.8)
49.5	50	Tin770	0.5	97.3(2.9)	89.7(2.9)	89.8(4.9)	28.1(0.7)	27.8(0.7)	27.4(1.2)
49	50		1	93.5(3.4)	92.0(4.2)	90.5(3.9)	27.3(0.3)	27.4(0.7)	27.5(1.0)
48	50		2	86.3(3.9)	78.1(0.3)	85.3(3.9)	23.8(0.8)	23.9(0.2)	23.7(0.3)
49.5	50	Chi81	0.5	85.7(3.3)	84.8(4.0)	84.7(2.7)	30.0(0.5)	28.4(0.1)	28.3(0.2)
49	50		1	86.4(1.1)	86.2(6.9)	85.7(2.4)	28.5(0.4)	26.8(0.6)	27.3(0.7)
48	50		2	83.1(1.2)	84.8(2.5)	85.4(3.1)	26.4(0.4)	25.2(0.8)	25.1(0.1)

decreased the tensile modulus and strength of the composites.

After 250 and 500 hr exposure, tensile modulus and strength of the unstabilized and stabilized composites decreased. The tensile modulus of stabilized composites was reduced indicating that the stabilizer was effective in minimizing in modulus caused by weathering. The most significant loss in modulus was for UV absorber (Chi81) stabilized composites. After 500 hr exposure, the PP potentially may undergo chain scission, resulting in lowered modulus. The tensile strength of UV absorber (Chi81)-stabilized composites was significantly greater than that of control and light stabilizer (Tin770)- and UV absorber (Tin360)-stabilized composites. The increase of UV absorber (Tin360) loading showed the increase of the stabilized composites, but this trend was not shown in Tin770 and Chi81 stabilized composites. Tensile strength decreased with increasing exposure up to 500 hrs. The observed loss in tensile properties can be probably explained by the loss in the ability of polymer to transfer stresses to the reinforcing fillers [3].

### 3.3. Surface degradation

To investigate the causes of the property reduction, several specimens were examined microscopically. Optical micrographs of the transverse and vertical surfaces were taken at 250 and 500 hr interval of exposure. It was noted that the wood fibers are visible on the exposed surface, and there is little bond between and polymer matrix [11]. The PP50WF50 composite exhibited noticeable fading and the oxidation. The observed changes can be attributed to the combination of the breakdown of lignocellulosic materials by UV light and the removal of this material by the water removal.

It is well known that PP is not stable to UV radiation [5]. With a large number of tertiary carbon sites, polypropylene is very sensitive to free radical formation and

decomposition by chain scission, resulting in the formation of lower molecular weight polymers on the surface. Wood flours also undergo UV degradation through free radical reactions with the lignin polymer in the cell wall. Swelling of the composites due to the presence of wood flours may result in an increase in surface area, allowing more material to be exposed to UV degradation. Figs. 3(a) to (h) show that the dark brown surface of the composites have undergone a noticeable color change due to UV radiation. The color change is from brown to be white that occurs at 250 to 500 hr exposure. The surfaces of all composites first show a slight surface roughness and then the surfaces started to turn white. By 250 hr of exposure, the surfaces are rough and a white powder can be removed from the surfaces with mild abrasion. At 500 hr of exposure, the surfaces are very rough and chalky. UV absorber (Tin360 and Chim81)-stabilized sample showed less whitening than control (PP50WF50) and light stabilizer (Tin770)-stabilized sample.

Figs. 4(a) to (h) represent the vertical edge of the composites after 250 and 500 hr exposure. An identifiable whitened layer appeared after weathering, which increased in depth with increasing exposure. The visible depth of degradation was greatest at the facial edges of the specimen and least in the middle of the specimen. UV absorber (Tin360 and Chim81)-stabilized sample showed thick degradation in depth than control (PP50WF50) and light stabilizer (Tin770)-stabilized sample.

## 4. Conclusions

A comparative analysis of the HALS and UVA and their respective photostabilizing effect on WPCs are reported in this study. UV absorbers were more efficient at preventing composite lightening than was UV

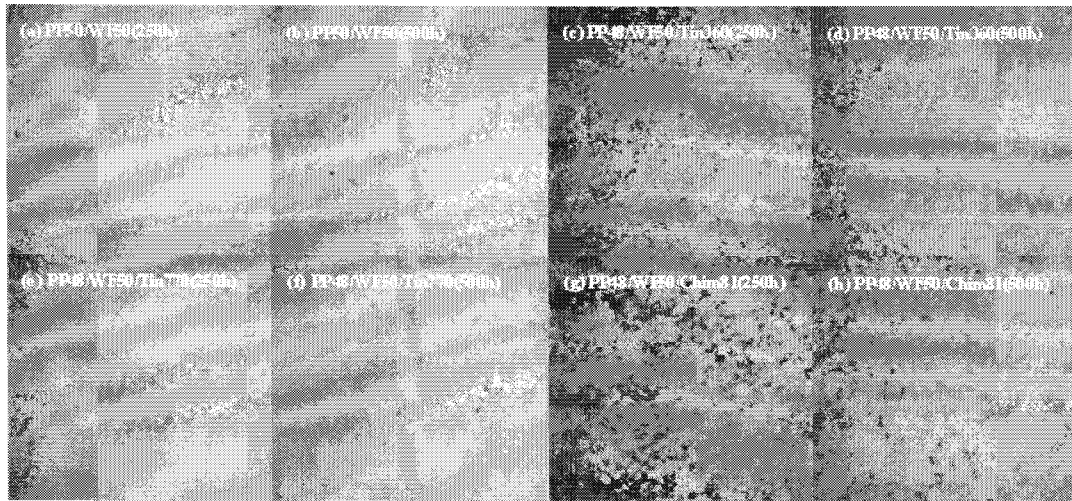


Fig. 3. Optical micrographs of surface of PP/WF composites after UV exposure of 250 and 500 hr.

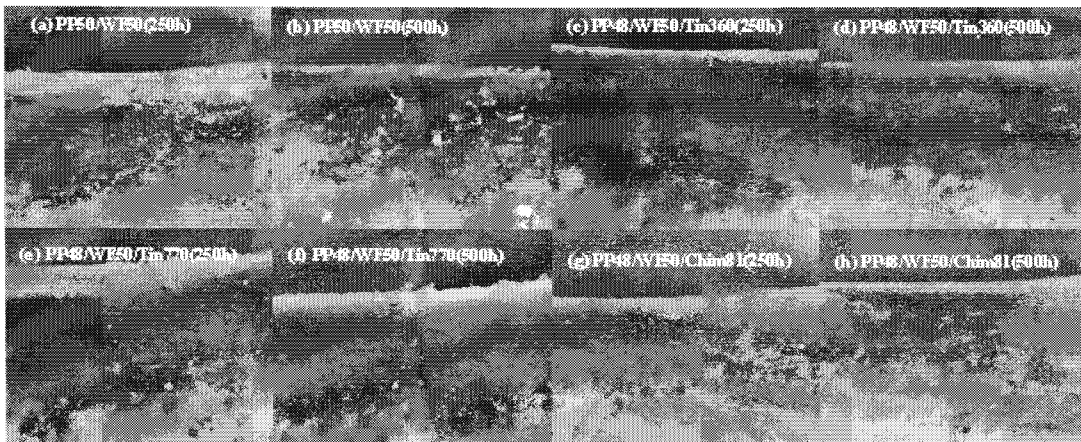


Fig. 4. Optical micrographs of vertical surface of PP/WF composites after UV exposure of 250 and 500 hr.

stabilizer. The amount of lightening decreased with the increase of UV absorbers and UV stabilizer. With the addition of a UV absorber (Tin360), the tensile modulus and strength of the composites increased slightly. However, the addition of a light stabilizer (Tin770) and a UV absorber decreased the tensile modulus and strength of the composites. After 250 and 500 hr exposure, tensile modulus and strength of the

unstabilized and stabilized composites decreased. The tensile strength of UV absorber (Chi81) stabilized composites was significantly greater than that of control and light stabilizer (Tin770)- and UV absorber (Tin360)- stabilized composites. UV absorber-stabilized samples showed less whitening and photodegradation than control and light stabilizer stabilized samples.

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