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Natural weathering properties of acetylated bamboo plastic composites

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ABSTRACT

The hydrophilic properties of lignocellulosic materials pose problems when they are used as reinforcement in plastics. The hydrophilicity of lignocelluloses influences its durability and also the interfacial adhesion between lignocellulose and polymers. Chemical modification, especially acetylation, has been used successfully to decrease the hydrophilicity and increase the weathering resistance of lignocellulose. Therefore, the purpose of this study is to investigate the natural weathering properties of bamboo plastic composites (BPCs) reinforced with bamboo fibers acetylated to different weight gains (WGs). The results showed that the retention ratios of mechanical properties of acetylated BPCs, especially those containing fibers with a high WG, were significantly improved as compared to the unmodified composite during natural weathering. In addition, the crystallinity of the high-density polyethylene (HDPE) in all BPCs increased after natural weathering for 120–240 days and then leveled off. This result indicates that the chain scission of HDPE mainly occurred during this period, producing shorter and more mobile chains and enabling them to undergo secondary crystallization. Furthermore, the mildew resistance of the acetylated BPCs was higher than that of unmodified composite. These results indicate that the durability and decay resistance of BPCs can be enhanced through acetylation of the bamboo reinforcement.

1. Introduction

In Asia, bamboo is a common natural resource and widely used as a raw material for construction, furniture, pulping, and handicrafts, which leads to many by-products (bamboo shavings and sawdust) from the bamboo-processing industry [1]. Of the many uses of these by-products, the manufacture of thermoplastic composites for applications as value-added panels is becoming popular [2–5]. In fact, wood plastic composite (WPC) is promoted as a lower-maintenance alternative to solid wood for various fixtures, such as window frames, fencing, roofing, decking, and siding [6]. The global WPC market has experienced double-digit growth in North America and Europe [7], and the demand for WPCs in the United States is expected to reach $2.4 billion in 2013 [8]. However, WPCs are composed of synthetic polymers and wood fiber, which experience photodegradation upon exposure to sunlight, especially ultraviolet (UV) [9,10]. Therefore, color fading, chalking, and strength weakening of WPCs may caused by weathering, restricting WPCs to specific outdoor applications.

The photodegradation of polymers originates from excited polymer–oxygen complexes, which are mainly produced by introducing catalyst residues, hydroperoxide groups, carbonyl groups, and double bonds during polymer manufacturing [11,12]. It has been shown that lignin is the constituent of wood that is most likely to undergo photodegradation, which leads to the radical induced depolymerization of lignin, hemicellulose, and cellulose at wood surfaces [13,14]. Furthermore, the majority of the strength loss in WPCs after weathering is caused by moisture effects [15]. Therefore, it is important to improve the photostability and hydrophobicity of wood to prevent fading and weakening of WPCs for outdoor applications [13,16,17]. It is well known that the weatherability and durability of wood products can be improved by acetylation [18–20]. Accordingly, it may be possible to improve the resistance of BPCs to photo- and bio-degradation by introduction of acetylated woody material into composites. To our knowledge, no prior report has assessed the weathering properties of WPCs made from acetylated bamboo fibers. Thus, the aim of this work is to demonstrate the effects of acetylation on the natural weathering properties of the BPCs.

2. Materials and methods

2.1. Materials

Makino bamboo (*Phyllostachys makinoi* Hayata) was provided by a local bamboo-processing factory, chipped and screened (16–24 mesh) without any pretreatment. HDPE (LH901) was purchased from USI Co. (Kaohsiung, Taiwan) with a melt flow index of

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0.95 g/10 min and a density of 953 kg/m^3. Acetic anhydride and dimethylformamide (DMF) were purchased from Sigma Chemical (St. Louis, MO, USA). The other chemicals and solvents used in this experiment were of analytical grade.

2.2. Acetylation

Bamboo fibers were immersed in a 20 mM solution of acetic anhydride in DMF with potassium carbonate (K_2CO_3) (1.1 mM) as a catalyst. The reaction was conducted at 100 °C and stirred for 1–2 h to obtain acetylated bamboo materials with different degrees of modification. At the end of the reaction, the acetylated bamboo fibers were washed with acetone and Soxhlet-extracted with acetone for 6 h. Finally, the acetylated bamboo was dried at 105 °C for 12 h, and the weight percent gain (WPG) calculated.

2.3. Composite processing

The BPCs were compression molded to 300 mm × 200 mm with 12 mm according to our previous research [1,21]. The weight ratio of the bamboo fibers (unmodified or acetylated) (moisture content < 3%) to HDPE powder was 60/40 (wt%). The expected density of the BPCs was 850 ± 50 kg/m^3. The BPCs were hot pressed at 200 °C for 8 min and then cold pressed until the temperature decreased to 25 °C (approx. 12 min).

2.4. Natural weathering test

Natural weathering tests were performed on composites facing south and inclined at a 45° angle, at the campus of National Chung Hsing University (24°07′25.7″ N, 120°40′30.7″ E) for a period of 1080 days, from November 2007 to November 2010. During the exposure period, the temperature ranged from 7.4 to 38.7 °C, and the average relative humidity was 75.0%. The exposed samples were periodically taken out and their properties measured.

2.5. Mechanical analysis

The flexural properties (MOR and MOE) of the composites were determined according to the Chinese National Standard CNS 2215. In brief, MOR and MOE data were obtained by the three-point static bending test with a loading speed of 10 mm/min and span of 180 mm (the specimen size was 230 mm × 50 mm × 12 mm). The samples were conditioned at 20 °C and 65% relative humidity for 2 weeks before testing. The MOR and MOE retention ratios of the BPCs after natural weathering were determined as follows: MOR (or MOE) retention ratio (%) = MOR_t (or MOE_t)/MOR_0 (or MOE_0) × 100, where MOR_0 (or MOE_0) and MOR_t (or MOE_t) are the MOR (or MOE) values of the composites before and after weathering, respectively, for time t.

2.6. Dynamic MOE analysis

The dMOE of the BPCs was evaluated by a nondestructive ultrasonic method [22] and wave velocities (V) were measured using a CT3 portable ultrasonic meter (Unipan-ultrasonic, Canada) at a frequency of 40 kHz. The dMOE of the BPCs was derived from the following equation: $dMOE = V^2 \times \rho$, where ρ is the bulk density [22,23]. The dMOE retention ratio of the BPCs after natural weathering was determined as follows: dMOE retention ratio (%) = $dMOE_t/dMOE_o \times 100$, where $dMOE_o$ and $dMOE_t$ are the dMOE values of the composites before and after weathering, respectively, for time t.

2.7. ATR-FTIR spectral measurements

The attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra of the BPCs were recorded on a Spectrum 100 FTIR spectrometer (Perkin–Elmer, UK) and a MIRacle ATR accessory (Pike Technologies, USA). Three spectra were acquired for each composite sample. The plastic index (PI) was calculated from the following equation: $PI = (I_{2916}/I_{897}) \times 100$, where I_{2916} and I_{897} represent the specific peak intensities of the HDPE and the bamboo, respectively [21]. In addition, the following regression equation relates the PI to a measurable HDPE content in the BPCs: HDPE content (wt%) = 9.9731 × PI + 23.366 ($R^2 = 0.993$).

2.8. Differential scanning calorimetry (DSC) thermal analysis

The thermal properties of the BPCs were measured using a DSC-7 (Perkin–Elmer, UK). The samples (1 mg) were heated from 50 to 250 °C at a rate of 10 °C/min under nitrogen. The crystallinity of the polymer matrix (X_c) was determined using the method described by Zou et al. [11] and calculated from the following equation: $X_c = \Delta H_m/\phi\Delta H_m^0 \times 100$, where ΔH_m is the experimental heat of fusion determined from the DSC measurement, ΔH_m^0 is the assumed heat of fusion of fully crystalline HDPE (293 J/g), and φ is the HDPE content (wt%) in the composites calculated from ATR-FTIR measurement based on the aforementioned equation ($\varphi = 9.9731 \times PI + 23.366$).

2.9. Measurement of surface color

The color parameters L^*, a^*, and b^* of the composite surface was measured using a spectrophotometer (Minolta CM-3600d, Japan) under a D_{65} light source with a test window diameter of 8 mm. Based on the CIE $L^*a^*b^*$ color system, L^* is the value on the white/black axis, a^* is the value on the red/green axis, b^* is the value on the yellow/blue axis, and ΔE^* is the color difference ($\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$).

2.10. Mildew resistance of composite

To compare the mildew resistance of the various specimens during natural weathering exposure, the degree of surface disfigurement of the composites by microbial growth was evaluated according to the ASTM standard D 3274 [24]. The colonization of the surface by mildew was rated from 0 to 10. A rating of 10 indicated a surface that was totally free of disfigurement by microbial growth, whereas a rating of 0 indicated the heaviest infestation.

2.11. Statistical analyses

All results were expressed as the mean ± SD. The significance of difference was calculated by Scheffe's test, and P values < 0.05 were considered to be significant.

3. Results and discussion

3.1. Color changes of the BPCs during natural weathering

The color variation of the unmodified and acetylated (WPG 8 and WPG 17) BPCs during 1080 days of natural weathering was evaluated. Fig. 1A shows that the ΔE^* values of all composites generally increased as the exposure time increased. However, the unmodified BPC exhibited no significant change in the first 56 days. Afterward, the value changed significantly, increasing linearly to 17.2 after 180 days of weathering and then leveling off. In contrast, the acetylated BPCs exhibited greater sensitivity to color change

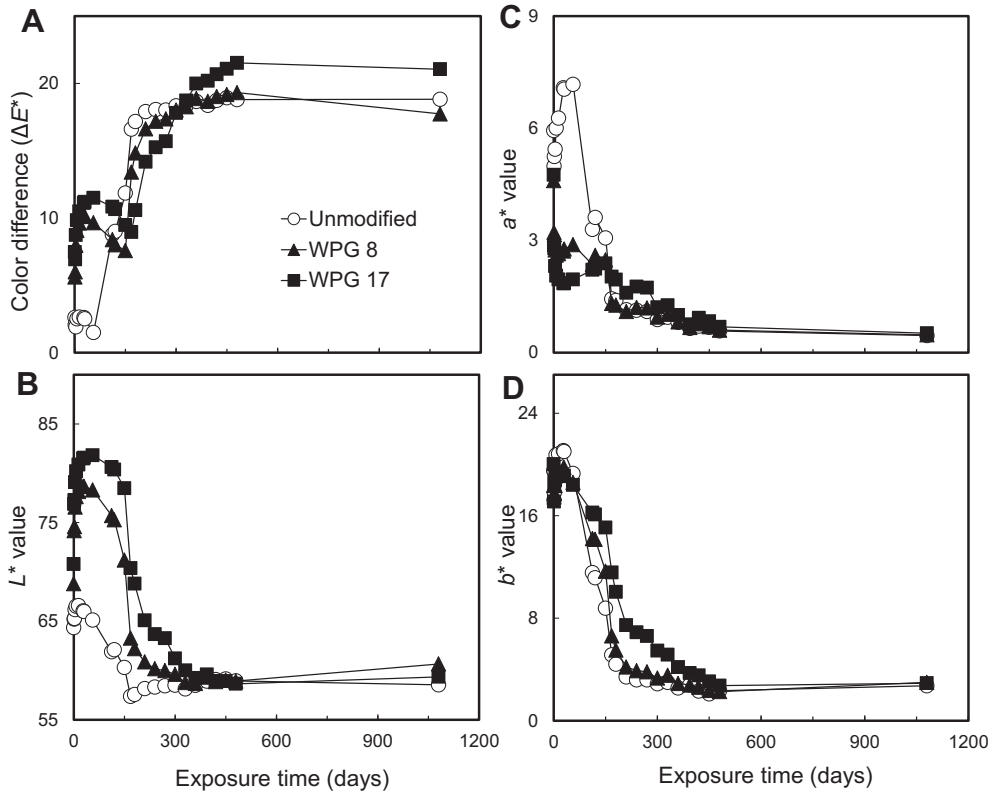

Fig. 1. Effects of acetylation on ΔE^* (A), L^* (B), a^* (C) and b^* (D) values of bamboo plastic composites after natural weathering for 1080 days. Mean values are shown ($n = 7$).

during the initial period of natural weathering. The ΔE^* values of the BPCs with fibers acetylated to WPG 8 and WPG 17 were 9.7 and 11.5 after weathering for 56 days, and they leveled off at 210 ($\Delta E^* = 17.9$) and 480 ($\Delta E^* = 21.5$) days, respectively. Fig. 1B shows the L^* value of the unmodified composite decreased significantly during natural weathering. This result differs from that obtained by Stark [15], who reported that lightening of WPC occurred during accelerated weathering. The L^* value of the unmodified composite was remarkably lower than that of the acetylated BPCs after weathering for periods of up to 180 days. In contrast, the b^* values of all BPCs exhibited no significant differences (Fig. 1D), but the a^* value of the unmodified BPC was higher than that of the acetylated composites for the same period of time (Fig. 1C). These results reveal that the surface color of the unmodified BPC was darker and redder than that of either of the acetylated BPCs. The unmodified BPC was colonized by the black mold (*Patellaria*-like) after 120 days of natural weathering (mildew resistance index change from unweathered 10 to 4, as shown in Fig. 5), but there was no significant difference in L^* values before ($L^* = 64.3$) and after ($L^* = 62.1$) weathering. Accordingly, color changes of the BPCs were not affected by the mold colonization. In addition, except for the acetylation level of bamboo, all of the BPCs had the same composition. Therefore, this result demonstrates that the unmodified bamboo was more susceptible to photooxidation than the acetylated bamboo. It is well known that among the constituents of lignocellulosic materials, lignin is most susceptible to photodegradation. It is a good UV absorber; therefore, the energy that is transferred in the range of 200–400 nm initiates the degradation process [25]. Most of the coloring substances generated by photooxidation of lignin come from further reactions between the intermediary phenoxy radicals and oxygen [26]. However, the acetylated BPCs retarded the browning process during natural weathering, in accord with results for acetylated veneer [18] and esterified wood [27]. These results suggest that the acetylation of lignocellulosic materials can play an important role in controlling the natural weathering process of BPCs.

3.2. Mechanical properties of the BPCs during natural weathering

The mechanical properties of the BPCs made from bamboo fibers acetylated to different levels are shown in Table 1. Despite a decrease in MOE values, BPCs with fibers acetylated to 8% and 17% WGs exhibited comparable flexural strength to the unmodified composite, and there was no significant difference on flexural properties for the different acetylated BPCs before weathering. However, the mechanical properties of the various BPCs varied as a function of the weathering time. The MOR and MOE retention ratios of the unmodified and acetylated BPCs decreased significantly during natural weathering (Table 1). Similar results were reported for the weathering of WPCs by Stark [15]. On the other hand, the retained MOR and MOE ratios of the acetylated BPCs (WPG 8 and 17) usually remained about 93% and 85–91%, respectively, after natural weathering for 1080 days. In contrast, the MOR and MOE retention ratios of the unmodified BPCs decreased significantly to 82% and 64%, respectively, after 480 days of natural weathering and then leveled off. The explanation for these observations is that the unmodified bamboo fibers swelled and shrank after absorbing and desorbing moisture. Such cyclic dimensional changes could produce cracks at the lignocellulosic material/polymer matrix interface [6], leading to the reduction of the MOR and MOE of the BPCs. However, the dimensional stability, hydrophobicity, and decay resistance of lignocellulosic materials can be significantly improved by acetylation [18–20,28–30], explaining the high strength retention for both acetylated composites over 1080 days of natural weathering. Furthermore, as shown in Table 1, the dMOE of all composites generally decreased with increased

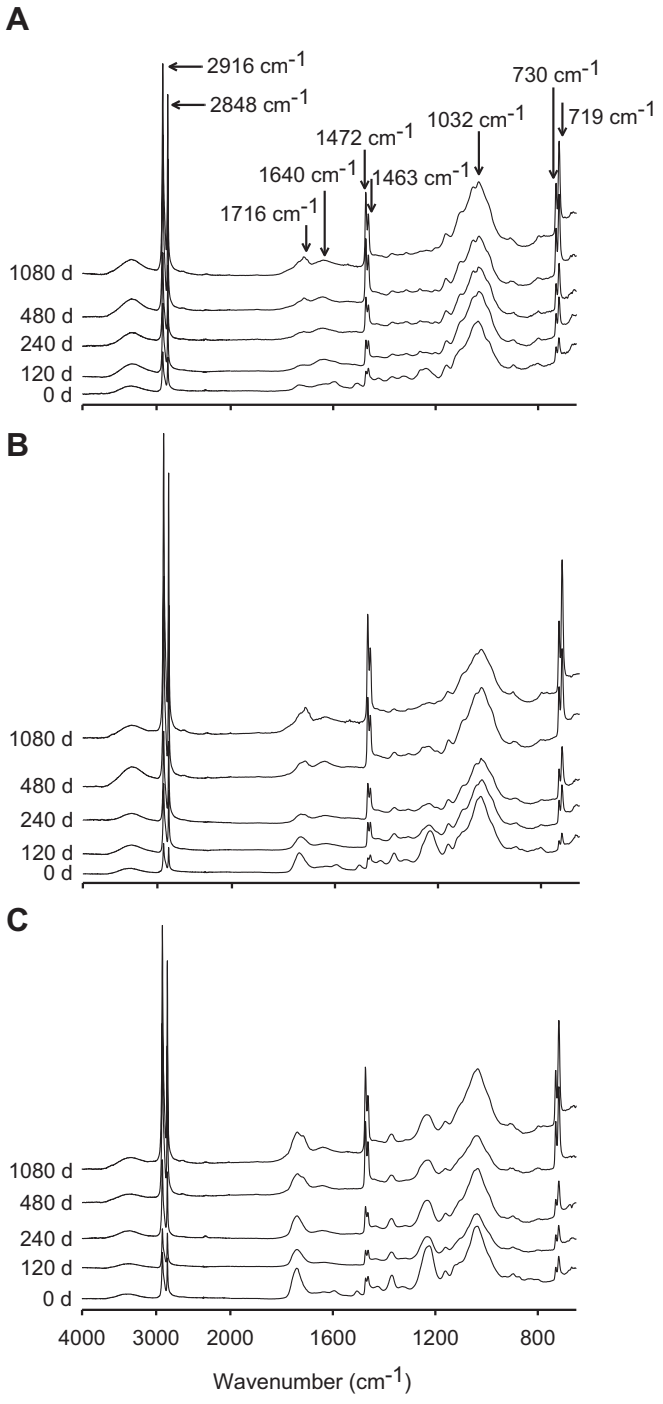

Fig. 2. Infrared spectra of various bamboo plastic composites after natural weathering for 1080 days. (A) Unmodified, (B) WPG 8, (C) WPG 17.

weathering. After 1080 days of exposure, the dMOE retention ratios of the BPCs containing bamboo fibers with various degrees of acetylation were, in decreasing order, WPG 17 (97%), WPG 8 (91%), and WPG 0 (unmodified) (71%). Of these BPCs, the composite containing fibers acetylated to 17% WG retained the greatest strength over the weathering period (there was no significant difference from the unweathered control), while the unmodified BPC retained the least. These results demonstrate that the mechanical strength of the BPCs for outdoor applications can be improved by reinforcement acetylation, especially with fibers acetylated to high WPG.

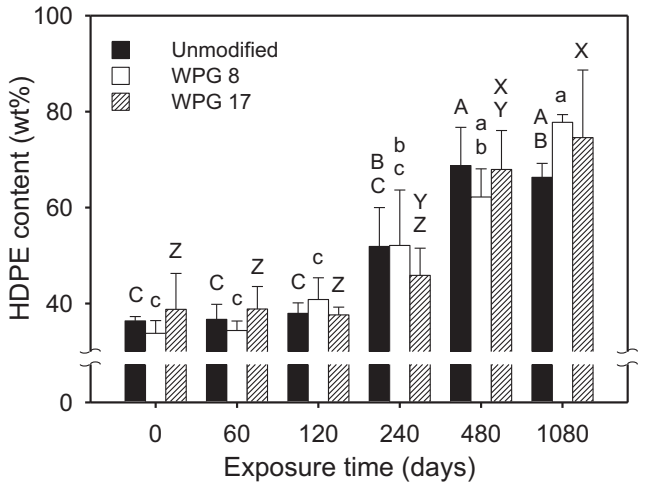

Fig. 3. Changes in HDPE content of bamboo plastic composites after natural weathering for 1080 days. Values are means ± SD ($n = 3$). Different letters indicate significant differences among groups at different exposure times ($p < 0.05$).

3.3. ATR-FTIR analysis of the BPCs during natural weathering

Under exterior exposure, it is well known that the chain scission of polyolefins can be induced by photodegradation via the Norrish I and II reactions, as indicated by an increase in the concentration of carbonyl and vinyl groups. FTIR spectroscopy was used to monitor chemical changes in BPCs during natural weathering. The FTIR spectra of various BPCs are shown in Fig. 2. The absorption band intensities corresponding to the carbonyl (1716 cm^{-1}) and vinyl (1640 cm^{-1}) groups of all BPCs increased with increasing exposure time. Others also found a similar increasing trend during the weathering of WPC [14,31]. This result confirms that the chain scission of the polymer matrix was independent of the degree of acetylation in bamboo during natural weathering. Additionally, the absorption bands at 2916 (asymmetric CH_2 stretching), 2848 (symmetric CH_2 stretching), 1472–1463 (CH_2 scissoring) and 730–719 cm^{-1} (CH_2 rocking) also increased significantly with increasing weathering time for all BPCs. Of these bands, the doublet peaks observed at 1472–1463 and 730–719 cm^{-1} correspond to the crystalline (1472 and 730 cm^{-1}) and amorphous zones (1463 and 719 cm^{-1}) of polyethylene [32]. In Fig. 3, the HDPE content of the

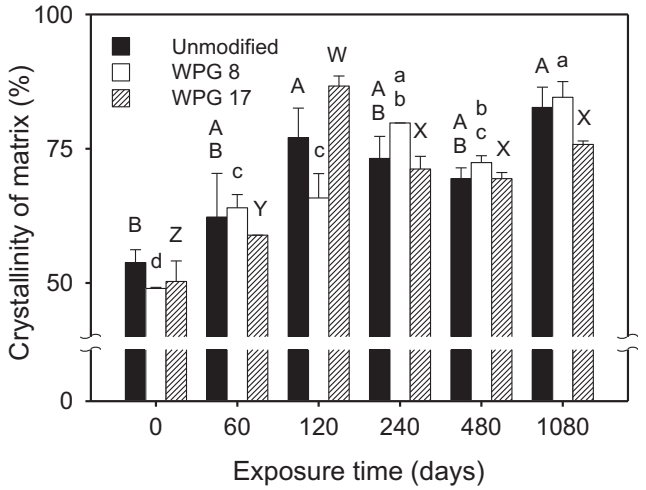

Fig. 4. Effect of acetylation on crystallinity of matrix of bamboo plastic composites after natural weathering for 1080 days. Values are means ± SD ($n = 2$). Different letters indicate significant differences among groups at different exposure times ($p < 0.05$).

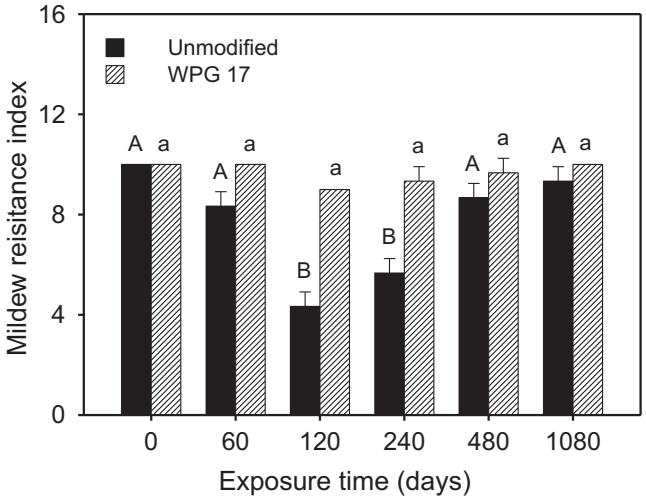

Fig. 5. Changes in mildew resistance index of bamboo plastic composites after natural weathering for 1080 days. Values are means ± SD ($n = 3$). Different letters indicate significant differences among groups at different exposure times ($p < 0.05$).

bulk composite was further determined as a function of the exposure time. The HDPE content of all BPCs exhibited no significant difference in the first 120 days of weathering, but the content gradually increased afterward from the original 40 wt% to 65–75 wt% until 1080 days of weathering. Accordingly, an explanation for the increasing trends of the methylene groups in the FTIR spectra is that bamboo located in the surface layer of the BPCs leach away during weathering, causing the plastic content to increase at the composite surface. These results suggest that acetylation did not significantly improve the photostability of the BPCs. Similar results have been obtained for other chemically modified wood [33–35].

3.4. Matrix crystallinity of the BPCs during natural weathering

The crystallinity of HDPE in the BPCs was determined as a function of weathering time (Fig. 4). The results demonstrate that the HDPE crystallinity of the composites significantly increased during the first 120–240 days of natural weathering, and a plateau was reached during further weathering to 1080 days, except for the BPC containing fibers acetylated to 17% WG. After 120 days weathering, HDPE crystallinity of the unmodified and WPG 17 BPCs increased from 54% and 49% to 77% and 87%, respectively. The highest crystallinity for the WPG 8 BPC matrix (80%) was obtained at 240 days of natural weathering. Zou et al. [11] reported that the crystallinity increase in the polyethylene during the initial weathering period was caused by chain scission in the amorphous phase of the polyethylene. The resulting shorter molecules are believed to produce sufficient chain mobility to cause secondary crystallization [36]. However, as chain scission continues to occur, it further affects the tie molecules, leading to a decrease in crystallinity. In Fig. 4, the crystallinity of the matrix of the BPC (WPG 17) decreased slightly as the weathering time increased from 120 days to 480 days. This decrease implies that the chain scission of the polymer matrix affected enough tie molecules to reduce the crystallinity during this period of weathering. It is well known that many reactions, including crosslinking and chain scission, can occur in polyolefins during weathering, leading to apparent differences in the crystallinity of samples. In other words, the crystallinity of the matrix could be used as an indicator to evaluate the photo-oxidative degradation of the polymer. Some literature reported that wood fibers or flours are effective photosensitizers (i.e. chromophore materials), and their incorporation into the polymer matrix promotes and/or accelerates photodegradation of the matrix [37,38]. Chemical modification is well known for reducing the photosensitivity of wood materials. However, in this study, there was no critical influence of acetylated fibers on the photostability of the matrix owing to the variations of matrix crystallinity during natural weathering. This seems to reveal that good photostabilty characterizes some modified wood materials, but generally not plastic composites reinforced with acetylated bamboo fibers.

3.5. The mildew resistance of the BPCs during natural weathering

It is well known that the hydrophilic nature of lignocelluloses increase water absorption, thickness swelling, and biological decay, leading to dimensional instability and biodegradation of composites. In this study, the water absorption and thickness swelling of the unmodified BPC were 19% and 4%, respectively, after 24 h of water immersion. In contrast, however, for acetylated BPCs, both values were less than 5% and 2%, respectively. This result indicates that the hydrophobicity and dimensional stability of BPCs could be enhanced through reinforcement acetylation. On the other hand, the variations in the mildew resistance of the specimens after exposure to the outdoor environment for 1080 days are shown in Fig. 5. The mildew resistance index of the unmodified composite decreased from 10 to 4 after weathering for 120 days. However, after 1080 days of weathering exposure, the mildew resistance index increased from 4 to 9. This phenomenon might be attributed to the removal of moldy bamboo fibers from the composite surface by leaching because the mildew resistance rate is completely congruent with the change of the HDPE content in Fig. 3. The more HDPE content on composite surface, the higher the mildew resistance of the BPC. In addition, the mildew resistance of the acetylated composite underwent no significant change during 1080 days of natural weathering. This result also reveals that acetylation can improve the mildew resistance of the BPC. Similar results were obtained by Papadopoulos [39] and Papadopoulos and Hill [40]. Papadopoulos and Hill [40] reported that the mechanism for decay protection in their case was blocking of the cell wall microcapillaries, which prevents access to cell walls by the low molecular weight degradative agents produced by fungi. Moreover, strength

Table 1
Effects of acetylation on strength and modulus retention ratios of bamboo plastic composites after natural weathering for 1080 days.

BPC	MOR (MPa)	MOR retention ratio (%)			MOE (GPa)	MOE retention ratio (%)			dMOE (GPa)	dMOE retention ratio (%)		
		0 day	480 days	1080 days		0 day	480 days	1080 days		0 day	480 days	1080 days
Unmodified	19.0^{A}	100.0^{a}	81.6^{b}	82.6^{b}	1.94^{A}	100.0^{a}	63.7^{b}	64.0^{b}	4.25^{A}	100.0^{a}	82.8^{b}	70.7^{c}
	(0.7)	(3.3)	(2.1)	(1.6)	(0.07)	(3.6)	(4.4)	(2.8)	(0.09)	(2.1)	(1.9)	(4.0)
WPG 8	18.1^{A}	100.0^{a}	91.5^{b}	92.8^{ab}	1.62^{B}	100.0^{a}	82.6^{b}	84.9^{b}	3.66^{B}	100.0^{a}	95.1^{b}	90.9^{b}
	(0.3)	(3.0)	(2.8)	(4.5)	(0.08)	(4.9)	(2.6)	(2.5)	(0.08)	(3.7)	(1.2)	(0.8)
WPG 17	17.7^{A}	100.0^{a}	95.2^{ab}	93.0^{b}	1.54^{B}	100.0^{a}	89.9^{b}	91.0^{b}	3.45^{C}	100.0^{a}	96.9^{b}	96.7^{ab}
	(0.5)	(2.5)	(3.0)	(1.9)	(0.04)	(2.9)	(3.2)	(3.7)	(0.04)	(2.2)	(1.9)	(0.2)

Values are means ($n = 3$). Values in parentheses are SD. Different capital and lower case letters indicate significant differences within a column and a row, respectively ($p < 0.05$).

losses in wood-based composite could be associated with attack by mold fungi [41]. This may be another reason why acetylated BPCs exhibited higher MOR and MOE retention ratios than the unmodified one after natural weathering for 1080 days (Table 1).

Fading, chalking, and strength weakening caused by environmental exposure are major problems for WPC in outdoor applications. In this study, acetylated BPCs had improved in mechanical properties and mildew resistance, but nor discoloration compared to unmodified BPCs when exposed to natural weathering. Previous research reported that darker color pigments, photostabilizers, and exterior coatings had a positive effect on the color stability and prevented chalking of WPCs [13,32,42]. Thus, a combination of chemical and physical treatments should be most effective in improving the overall weatherability of the composites, and it would be worth investigating in future studies.

4. Conclusions

Bamboo plastic composites were successfully prepared by the manufacturing method of forming and flat pressing similar to conventional particleboard production. Acetylation of bamboo reinforcement is a useful method to improve the weathering properties of BPCs. Of all BPCs, the composite made from high degree of acetylation of bamboo fibers exhibited superior MOR and MOE retention ratios after 1080 days of natural weathering, while the unmodified BPC had the lowest ratios. However, chain scission of the polymer matrix occurred in all BPCs during natural weathering, and no significant differences were observed between the composites, which indicated that the matrix degradation was independent of the acetylation level of reinforcements. In addition, acetylated BPCs exhibited better mildew resistance than the unmodified one, but color fading was observed in all composites. Thus, future studies should focus on the color stability of the acetylated BPCs during natural weathering, and the creep behaviors of specimens should also be evaluated.

Acknowledgments

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