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Improving thermo-oxidative degradation resistance of bamboo fiber reinforced polypropylene composite with antioxidants. Part I: Screening of antioxidants

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ABSTRACT: In this study, the effect of antioxidant application (applied in different combinations, ratios and contents) on the thermo-oxidative degradation resistance of bamboo fiber polypropylene composites (BFPCs) were investigated, with oxidative induction time (OIT), weight loss, surface color, and flexural mechanical properties as the main indicators for evaluation. The results showed the addition of antioxidants could greatly increase the OIT and reduce the weight loss and color change of the composites after 900 h of thermal weathering. Meanwhile, the flexural mechanical properties were little affected or even slightly improved. The combination of 1076 and DLTP antioxidants at a ratio of 2:1 and 0.2 wt % content was found to exhibit the best thermal oxidation resistance with respect to the OIT, mechanical properties and cost. Our study indicate that the OIT can serve as a simple and quick indicator for the evaluation of thermo-oxidative resistance of BFPC. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 44198.

KEYWORDS: antioxidants; bamboo fiber polypropylene composites (BFPCs); oxidative induction time; thermal weathering

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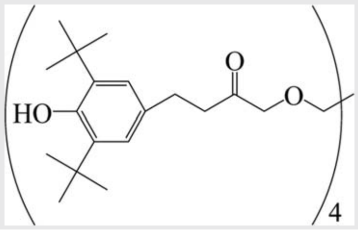
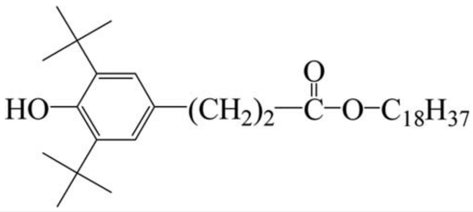
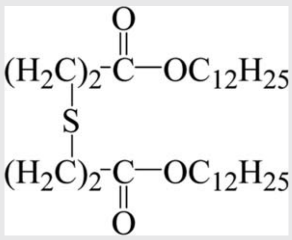
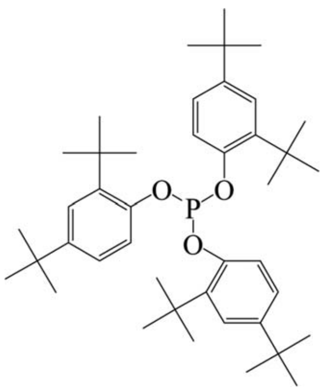
INTRODUCTION

Wood-plastic composites (WPCs) have gained popularity worldwide due to their wide applications and various advantages including: resistance to biodegradation, dimensional stability, low cost and easy maintenance, recyclability, eco-friendliness, and good mechanical properties.[1] However, the increasing outdoor application of WPCs are providing more evidences for the necessity to increase its resistance to weathering in the long-term.[2] WPC products that are used outdoors, either on the ground or aboveground, are subject to accelerated deterioration[3] from factors including fungi, termites,[4] ultraviolet rays, high temperature, oxygen, air pollutants, and moisture.[5] Likewise, WPCs tend to discolor when exposed outdoors, leading to a degradation in their esthetics and mechanical properties.[6]

Several additives, such as pigments,[7] nano TiO_2 and ZnO,[8,9] and photo-stabilizers[10] have been used to improve the weathering resistance of WPCs. The enhancement of interfacial adhesion[11,12] and cellulose graft copolymerisation[13–15] have also been proposed. These methods can reduce color fading and the degradation of mechanical properties. Antioxidants were widely used in polymer composites[16,17] as an effective filler material to decrease oxidative damage mediated by free radicals.[18] Antioxidants can be divided into primary and secondary antioxidants depending on their mode of operation. Hindered phenols are a type of primary antioxidant, which inhibit oxidation by donating a hydrogen atom.[19] Secondary antioxidants are typically sulfur or phosphorous-based compounds and can decompose peroxides that serve as intermediate products in oxidation reactions. When primary and secondary antioxidants are used together in polymer stabilization, positive synergism tends to occur.[20–22] However, little information regarding the effect of antioxidants on the thermo-oxidative degradation resistance of natural fiber reinforced plastic composites is currently available.

Bamboo is widely planted and used in China. It is one of the fastest growth plants in the world and can be used for many purposes. The extraordinary mechanical properties of bamboo mainly stem from its fiber components.[23] Bamboo fibers (BFs) are comparable to synthetic fibers (such as glass fibers) because of their relatively low cost, renewability, biodegradability, accessibility and high aspect ratio.[24] Furthermore, it is much safer to work with bamboo than glass fibers during the manufacturing process, because the latter produces tiny glass particles that are harmful to the human body.[25] BFs, therefore, have great

Table I. Antioxidants Structures and Characteristics

Name	Structure	Molecular weight
1010		1178
1076		531
DLTP		514
168		647

potential for replacing synthetic fibers in the production of fiber-reinforced composites, as has been illustrated by the increasing number of academic papers published in this area in the last decade.[26–28]

In this two-paper serious study, we focused on the effect of antioxidants application on the thermo-oxidative degradation resistance of bamboo fiber polypropylene composites (BFPC). In the first part, the effect of various combinations of primary antioxidants (Irganox 1010 and 1076) and secondary antioxidants (Irgafos 168 and dilaurylthiodipropionate DLTP), ratio, and contents was studied with oxidation induction time (OIT) as the main indicator for evaluating the thermo-oxidative degradation resistance. Accelerated thermal weathering test of the BFPC was also carried out and the weathering behavior was described by weight loss, color change and also with a flexural properties test. The objective of this part is to identify the suitable antioxidants for BFPCs and provide a more comprehensive understanding of how antioxidants are correlate to the thermo-oxidative degradation resistance of BFPC. In the second part of this study, the effect of antioxidants on other selected fundamental properties of BFPCs (such as water absorption, thermal stability, and crystallinity) and dynamic mechanical properties were studied.

EXPERIMENTAL

Materials

Industrial BFs with 100 mesh were obtained from Hubei Sanmu Wood Technology (China). Isotactic polypropylene (PP) and maleated polypropylene polymer (MAPP) powders with a particle size of less than 180 μm were purchased from Shanghai Li Yang Mechanical and Electrical Technology (China). The densities of PP and MAPP were 0.91 g/cm^3 and 0.90 g/cm^3, respectively. For MAPP, the grafting percentage was 1%. Irganox 1010 (pentaerythrityl-tetrakis- (3,5-di-*tert*-butyl-4-hydroxyphenyl propionate), Irganox 1076 [n-Octadecyl-β-(4-hydroxy-3,5-di-*tert*-butyl-phenyl

Table II. Formulations of BFPCs

Sample code	PP (%)	BF (%)	MAPP[a] (%)	Ratio[b]			
				1010	1076	DLTP	168
1-1	55	45	6	0	0	0	0
2-1	55	45	6	2	0	1	0
2-2	55	45	6	1	0	1	0
2-3	55	45	6	1	0	2	0
3-1	55	45	6	2	0	0	1
3-2	55	45	6	1	0	0	1
3-3	55	45	6	1	0	0	2
4-1	55	45	6	0	2	1	0
4-2	55	45	6	0	1	1	0
4-3	55	45	6	0	1	2	0
5-1	55	45	6	0	2	0	1
5-2	55	45	6	0	1	0	1
5-3	55	45	6	0	1	0	2
[c]6-1	55	45	6	0	2	1	0
[d]6-2	55	45	6	0	2	1	0
[e]6-3	55	45	6	0	2	1	0

[a] Means the MAPP based on the weight of PP matrix.
[b] Represents the total content of antioxidants at 0.4 wt % based on the weight of PP matrix in code 2-5.
[c–e] Indicate the total content of antioxidants at 0.2 wt %, 0.55 wt %, and 0.75 wt % based on the weight of PP, respectively.

propionate], Irgafos 168 (Tns-(2,4-di-*tert*-butyl)-phosphite), and DLTP were purchased from Beijing Additives Institute (China). The structure and characteristics of these antioxidants are described in Table I.

Composite Processing

BFs were dried for 6 h at 103 ± 2 °C until the moisture content decreased to less than 3%. BFs, PP, MAPP, and antioxidant particles were mixed in a high-speed mixing machine for 90 min at 100 °C. The BFPCs were subsequently compression molded at 180 °C for 10 min at 6 MPa to dimensions of 250 mm × 90 mm × 3.5 mm (3895, CARVER). The weight ratio of BFs to PP powder was maintained at 45/55 (wt %) and MAPP at 6 wt % (based on PP matrix). The specific formulations are presented in Table II.

OIT Test

The thermo-oxidative stability of a polymer can be assessed based on its OIT, which is measured with a differential scanning calorimeter (DSC). OIT is the time when the onset of thermal oxidation occurs in the melt.[26] Normally, the more resistant the sample is to oxidation, the longer is the OIT. Samples, in the form of rectangular sheets, were cut from the cross-section of the prepared composite using a sliding microtome. Each sample had dimensions of 4.5 mm × 3.5 mm ×0.3 mm and weight of ~8 mg. Samples were placed in a clean open aluminium pan after drying at 103 ± 2 °C for 4 h. An empty pan was used for the reference. The sample and reference pans were heated using a DSC from 30 to 190 °C at a rate of 20 °C per minute, under a constant flow of nitrogen introduced at a rate of 50 mL per minute (TA Q 100, TA Instruments). After thermal equilibration (5 min) occurred at the preset temperature, the pans were exposed to pure oxygen (at a flow rate of 50 mL per minute) until an exothermal reaction occurs (or until 60 min was reached). The OIT was measured as the time corresponding to the point at which the extrapolated exothermal curve intersects the extended baseline.[29] Six replicates of each formulation were tested.

Thermal Weathering

The prepared BFPCs were conditioned at 23 ± 2 °C and relative humidity of 50 ± 5% for 40 h according to ASTM D 618. Subsequently, the composites were subject to thermal weathering using a common oven at 100 °C for 900 h. The weight loss, surface color change, and flexural mechanical properties were tested before and after thermal weathering.

Weight Loss

Weight loss (%) was calculated according to eq. (1):

$$\text{Weight loss} = \frac{M_2 - M_1}{M_1} \times 100 \quad (1)$$

where M_1 and M_2 are the oven dried (6 h at 103 ± 2 °C) weight of the composites before and after thermal weathering.

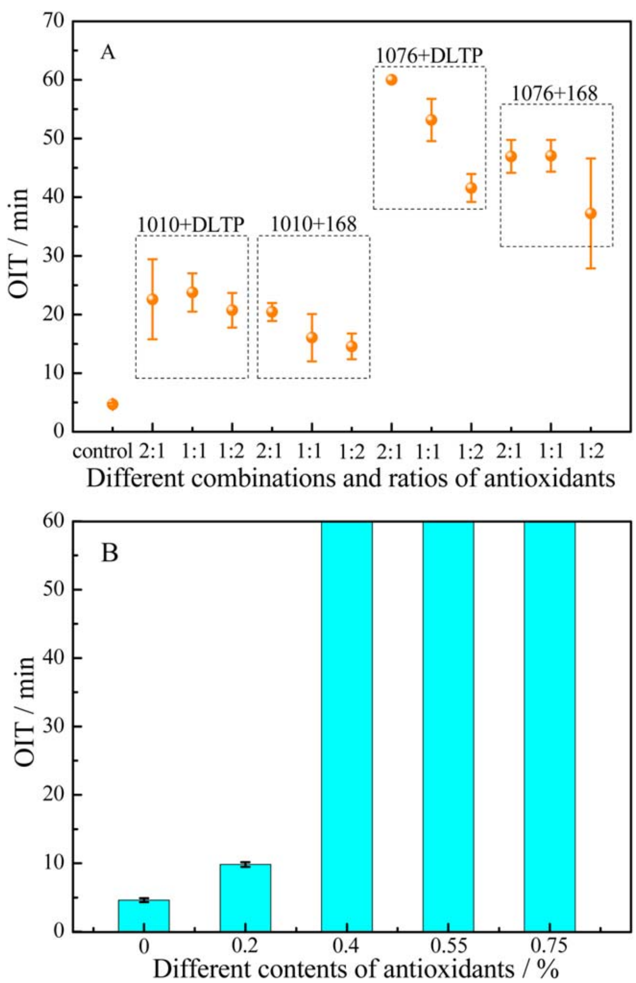


Figure 1. The effect of different combinations and ratios (A), and contents (B) of antioxidants on the OIT of BFPCs (tested at 190 °C). (B: the ratio of 1076 and DLTP was 2:1). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Surface Color Change

Color stability is considered to be a very important aesthetic property for the final consumer of WPCs. In some cases, it is even the determining factor for the selection of products. The surface color of the weathered and control samples were measured using a chroma meter (Spectro-guide sphere gloss, BKY). The CIELAB color system was used to measure the surface color in L^*, a^*, and b^* coordinates. L^* represents the lightness coordinate and varies from 100 (white) to 0 (gray); a^* represents the red ($+a^*$) to green ($-a^*$) coordinate; and b^* represents the yellow ($+b^*$) to blue ($-b^*$) coordinate. The color difference was calculated as outlined in ISO 7724 according to the following eq. (2):

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \tag{2}$$

where ΔL^*, Δa^*, and Δb^* represent the difference between the initial and final values of L^*, a^*, and b^*, respectively. The surface color of six replicates was measured at five locations on each composite sample.

Flexural Mechanical Properties

Flexural mechanical tests were carried out according to ASTM D 790 with a micromechanical tester (5848, Instron, Norwood, MA). In brief, flexural mechanical data was obtained by a three-point static bending test with a loading speed of 0.2 mm/min and span of 48 mm (the specimen size was 64 mm × 14 mm × 3.5 mm). At least five replicate specimens were tested for each formulation.

Statistical Analyses

To determine the effect of the combinations and ratios of antioxidants on the OIT, as well as the effect of thermal weathering on the properties of BFPCs, a two-sample analysis of variance (ANOVA) was carried out with an α significance value of 0.05. Moreover, the effect of contents of antioxidants on BFPCs was conducted on a one-sample ANOVA with the same α significance value. All statistical analyses were performed using the PASW Statistics 18.

RESULTS AND DISCUSSION

Short-Term OIT of BFPC

Figure 1 shows the effect of different combinations, ratios and contents of antioxidants on the OIT of BFPCs. The OIT of BFPC without any antioxidant was as low as 4.7 ± 0.3 min. All of the various combination and ratio of antioxidants significantly increased the OIT to over 14 min ($p < 0.01$, One-way ANOVA), among which the combination of 1076 with DLTP demonstrated the best performance with an OIT of as high as over 60 min. Similar values were also reported in other studies. Farhadinejad *et al.*[30] recorded an OIT of wood/PP composite at about 23 min. Gadioli *et al.*[31] reported that Eucalyptus cellulose fibers treated with different levels of bleach reinforced PP composites at an OIT ranging from 5.9 to 8.8 min. This difference was reasonable due to the differences in composition, types of polymer matrix and fillers, as well as the resultant interfacial zone and internal stress factors during fabrication.[32] Normally, the OIT of WPC tested at 190 °C should be longer than 10 min to ensure a service life of 10–15 years.[33] Therefore, it is

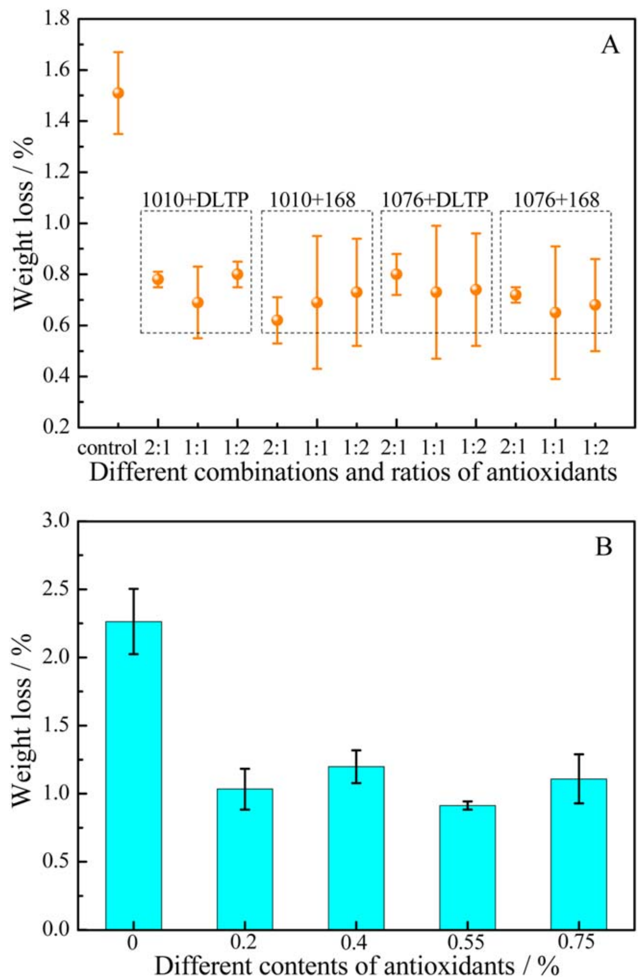


Figure 2. The different combinations and ratios (A), and contents (B) of antioxidants on the weight loss of BFPCs after 900 h of thermal weathering. (B: the combination of 1076 with DLTP was set at a ratio at 2:1). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

necessary for the production process of BFPCs to include the addition of antioxidants to provide a prolonged service life, especially when the final product will be used outdoors. Therefore, the OIT test is a simple and fast method for screening appropriate antioxidants that can be used in the production of natural fiber polymer composites.

It is obvious that the OIT value of BFPCs with 1076 as the primary antioxidant was significantly higher than that 1010 ($p < 0.01$, two-way ANOVA, LSD multiple comparisons), due to the easy release of low-molecular antioxidants like 1076 from the polymer matrix, which arises from migration, evaporation and extraction.[34,35] Nevertheless, contrasting results were found for the pure PP polymer, where a higher molecular weight of antioxidant resulted in a longer OIT.[36] This was probably attributed to the complex interaction among BFs, antioxidants, and the PP matrix. The OIT values generally decreased with an increase in secondary antioxidant concentration, except for the combination of 1010 and DLTP at a ratio of 1:1 [Figure 1(A)]. This demonstrated that the primary antioxidants played a dominant role in the anti-thermo-oxidation of BFPCs. Moreover,

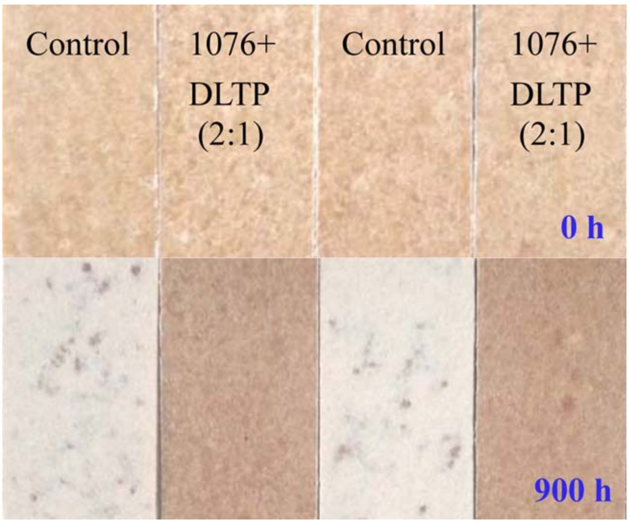


Figure 3. Digital photographs of BFPCs before and after 900 h of thermal weathering. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the OITs for BFPCs treated with DLTP and synergized with 1076 or 1010 was slightly longer than 168. The main reason for this should be the difference in their structures. DLTP contains two long chain alkyls, which makes it easier to decompose

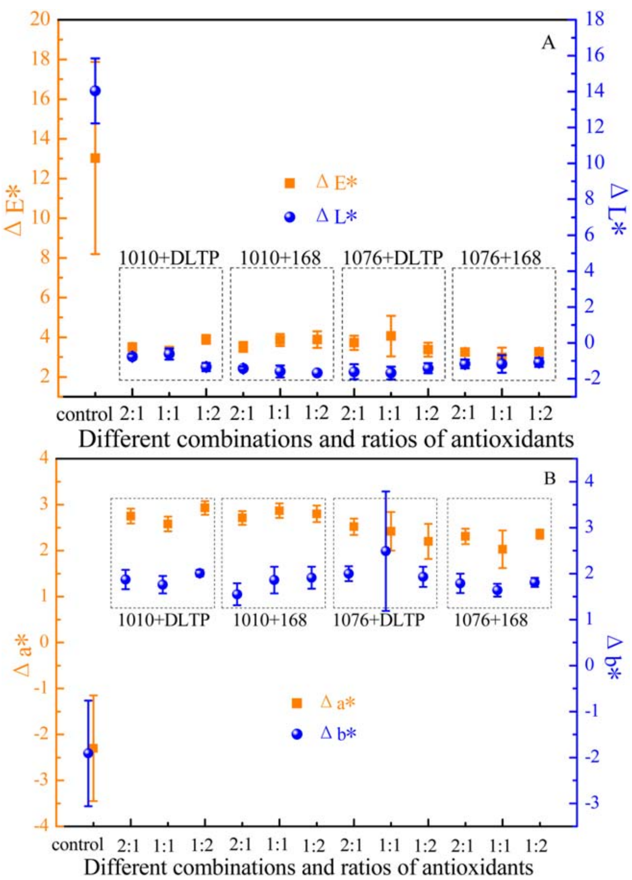


Figure 4. The effect of different combinations and ratios of antioxidants on the color change of BFPCs after 900 h of thermal weathering. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

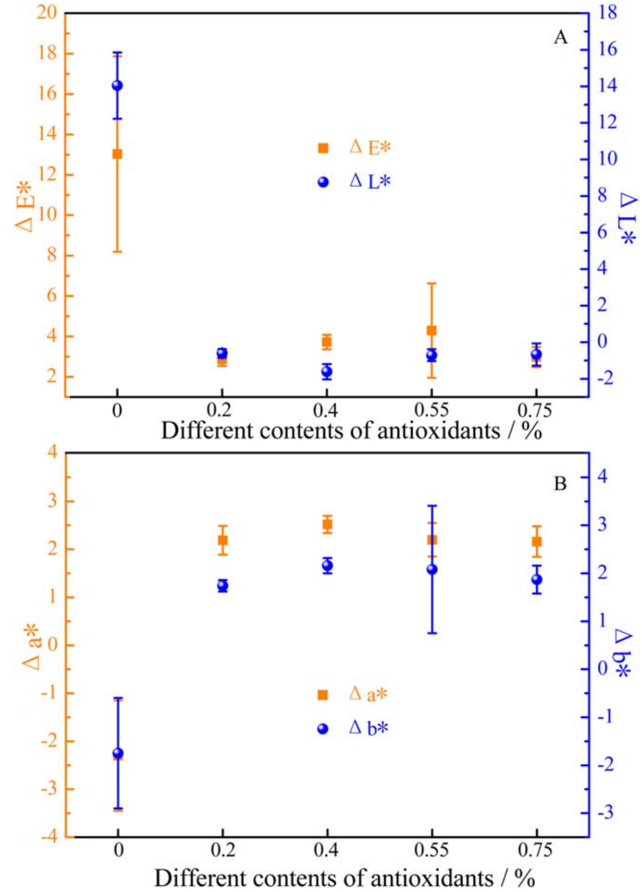


Figure 5. The effect of different contents of antioxidants on the color change of BFPCs after 900 h of thermal weathering. (Note: the combination of 1076 with DLTP was set at a ratio of 2:1). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

peroxides that are intermediate products in the oxidation reactions when compared to the aromatic structure in 168. It could, therefore, be safely concluded that the combination of 1076 and DLTP, especially at a ratio of 2:1 is a suitable antioxidant combination for BFPCs.

OIT significantly improved with the increasing content of antioxidants ($p < 0.01$, one-way ANOVA), as shown in the case of 1076 and DLTP at a ratio of 2:1 [Figure 1(B)]. The addition of 0.4 wt % 1076 and DLTP combination resulted in an OIT value higher than 60 min and, therefore, an higher concentration was unnecessary. The same trend was also found in previous studies,[29,37] where the percentage of antioxidants by weight commonly used by manufacturers for polymeric geomembranes was less than 0.5%,[38] whereas it increased to more than 0.5% only recently.[39] In this case, an antioxidant amount of 0.4 wt % is recommended based on the OIT value.

Weight Loss

Weight loss after thermal weathering can be used to evaluate the thermo-oxidative degradation resistance of WPCs. For the control samples, the weight loss was 1.51% after 900 h of thermal weathering, while values sharply decreased to less than 1% after the addition of antioxidants [Figure 2(A)]. Despite the fact

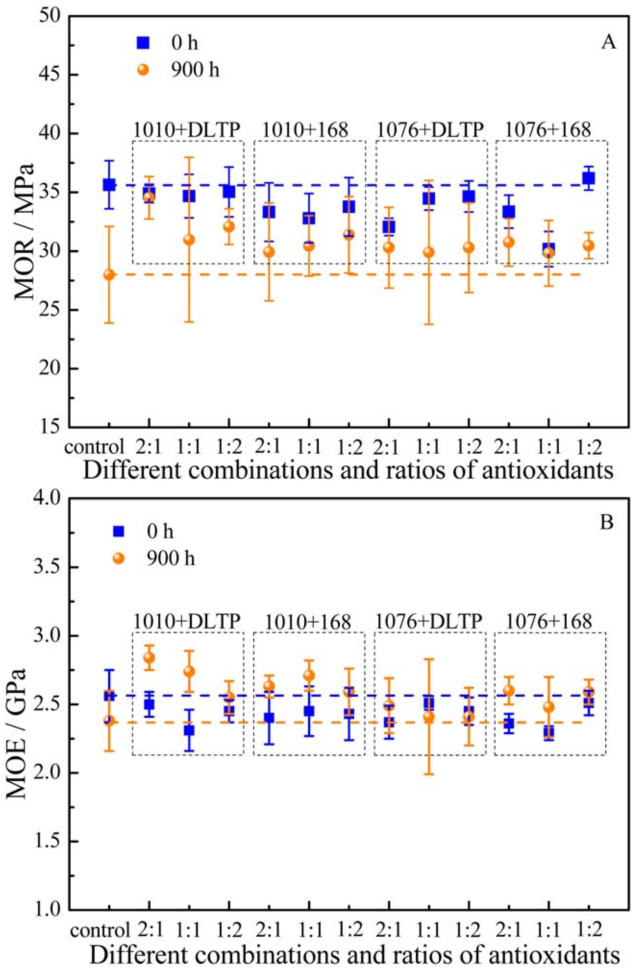


Figure 6. MOR (A) and MOE (B) change of BFPCs with different combinations and ratios of antioxidants after 900 h of thermal weathering. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

that different combinations and ratios have a significant effect on BFPC weight loss ($p_{combinations} < 0.05$, $p_{ratios} < 0.05$, two-way ANOVA), the difference in absolute average values was small. Moreover, the weight loss of BFPCs with varying contents of antioxidants decreased significantly by approximately 51.0% compared with control composite ($p < 0.01$, one-way ANOVA) as seen in Figure 2(B), while the weight loss of BFPCs was unaffected with increasing the contents of antioxidant ($p = 0.06 > 0.05$, one-way ANOVA).

For all fiber reinforced polymer composites, oxidation reaction-diffusion phenomena will take place within the polymer matrix when they are exposed to elevated temperatures for a long period of time.[40] The subsequent chain scission can lead to weight loss in the matrix.[41,42] Zhang *et al.*[43] found that the changes of weight for carbon fiber/epoxy composites were less than 1% after 160 thermal aging cycles. They attributed the weight loss to the major out-gassed products of H_2O, N_2, and hydrocarbon. Therefore, the minimal weight loss for BFPCs incorporated with certain antioxidants indicated that the antioxidants were useful for reducing chain scission in the PP polymer.

Color Analysis

Figure 3 shows the color change in BFPCs with and without antioxidants after 900 h of thermal weathering. All samples show a similar color before thermal weathering, indicating that a small amount of antioxidant treatment has little effect on the appearance of the composites. Interestingly, the discoloration of the control and treated samples were vastly different, where the former underwent obvious fading while the latter became only slightly darker with no effect on overall aesthetics.

Figures 4 and 5 show the quantitative change in BFPC color with different antioxidants after 900 h thermal weathering. The ΔE^* value of the control composites was over three times higher than those with the addition of antioxidants. The ΔL^*, Δa^*, and Δb^* values for the control samples were completely opposite to the ones with the addition of antioxidants. These results revealed that the surface color of the modified BFPCs was darker, redder, and yellower than that of the control samples. Moreover, the effect of different antioxidants on the surface color change for BFPCs was statistically significant, where $p_{contens,\Delta L^*} < 0.01$ for example (One-way ANOVA). However, the absolute ΔE^* was less than 5, indicating that only a minimal color change occurred for samples treated with antioxidants.

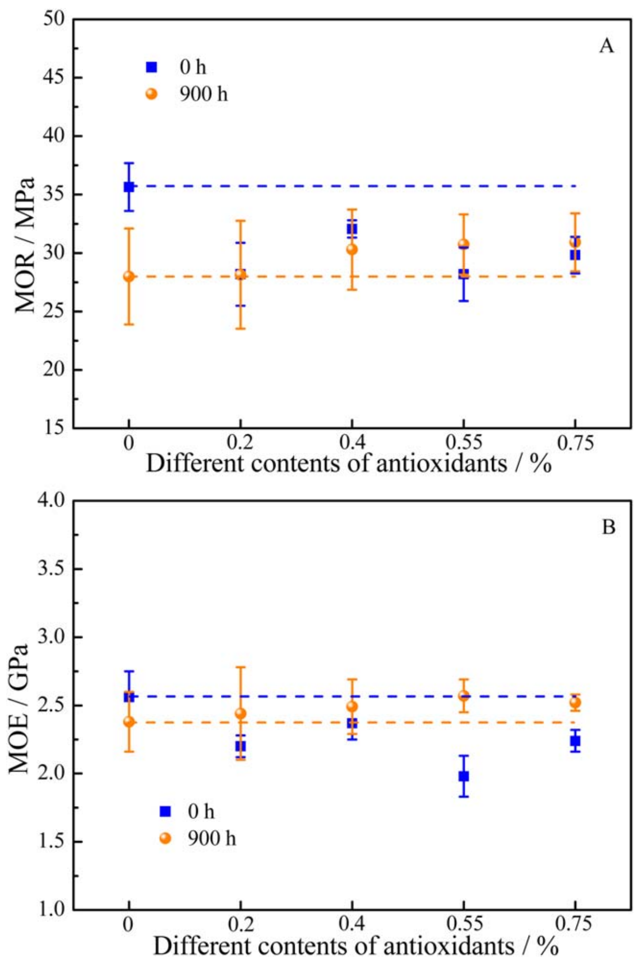


Figure 7. MOR (A) and MOE (B) change of BFPCs with different contents of antioxidants after 900 h of thermal weathering. (Note: the combination of 1076 with DLTP was set at a ratio of 2:1). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The color change of BFPCs after thermal weathering is mainly attributed to the constituents of bamboo fillers. Hot air treatment affects the chemical composition of bamboo by degrading both cell compounds and extractives.[44] As a result, the color of bamboo becomes darker compared to the untreated sample, which is primarily due to the formation of benzoquinone by surface oxidation.[45] Moreover, the color change of BFPCs is also correlated to the PP matrix. On the one hand, PP polymer can cause yellowing after thermal weathering for as low as 7 h, mainly due to the formation of chromophores such as carbonyl groups;[21,36] on the other hand, the antioxidant-containing PP also leads to incremental yellowing ascribed to the formation of yellow and red conjugated diene compounds, formed as a consequence of the sacrificial trapping of alkylperoxy radicals by phenolics.[46] Furthermore, the slight darkening of BFPCs treated with certain antioxidants was probably due to the formation of colorless aryl phosphates through the reaction between antioxidants and quinones.[47] However, for BFPCs without any antioxidant treatment, color fading following prolonged thermal weathering cannot be explained by the above theory. It is speculated that chromogenic lignin components tend to degrade into smaller fragments without the protection of antioxidants after prolonged thermal treatment.

Flexural Property Analysis

Figures 6 and 7 exhibit the variation of flexural properties of BFPCs with the addition of antioxidants before and after 900 h of thermal weathering. The MOR and MOE of BFPCs with various combinations of antioxidants only decreased slightly or even increased in comparison to the control samples. The retention ratios of MOR and MOE (MOR or MOE retention ratio (%) = $MOR_{900\ h}$ or $MOE_{900\ h}/MOR_{0\ h}$ or $MOE_{0\ h} \times 100$) of BFPC without any antioxidant were 78.5% and 93.0%, respectively. This value increased to a range of 84.1 to 109.4% for MOR and 96.0 to 129.8% for MOE with the addition of different antioxidants. It is well known that chain scission occurs when PP is exposed to sunlight or high temperatures. Shorter mobile molecular chains will recrystallize at the initial stage,[48] resulting in improved crystallinity and flexural properties.[49] However, continuing chain scission will eventually damage PP and lead to MOR loss in WPCs.[49,50] The addition of antioxidants can reduce the occurrence of free radicals and mitigate the radical-based oxidative process, which will definitely favor the preservation of MOR in BFPCs. It is interesting to note that the MOE of BFPCs with the addition of antioxidants after 900 h of thermal weathering was normally a little higher than the composites before thermal weathering, except for a slight decline in the antioxidant combination of 1076 and DLTP at ratios of 1:1 and 1:2. During thermal weathering, cross-linking reactions may also take place as a competitive mechanism to chain scission. This kind of cross-linking originates from the superposition of peroxide degradation and polymer degradation via C—C breakages and chain transfers.[35] Many studies reported that cross-linkages were accompanied by a positive effect on the modulus of composites.[41] Therefore, the enhancement of MOE for BFPCs treated with different antioxidants after thermal weathering indicates that the added antioxidants are involved in the process of cross-linkages. Furthermore, 1010 seems to perform better in maintaining the MOR of BFPCs compared to 1076, which could be explained by the relatively slower degradation rate for the antioxidant with a higher molecular weight.[35]

Based on the above, the antioxidant combination of 1076 and DLTP at a ratio of 2:1 had the highest OIT value and demonstrated the strongest resistance against thermo-oxidative degradation, including weight loss, color change and mechanical retention. A content of 0.2 wt % or slightly higher (such as 0.3 wt %) can be considered as a suitable concentration of antioxidant for BFPC production, if the manufacturing cost needs to be considered.

CONCLUSIONS

In this study, the resistance of BFPCs against thermo-oxidative degradation with the addition of different commercial antioxidants was investigated, which led to the following conclusions:

1. The OIT of the control BFPC was 4.7 ± 0.3 min, which was lower than the required 10 min to ensure a 10–15 year service life for WPCs. BFPCs treated with all combinations of antioxidants significantly increased OIT, among which the 1076 and DLTP combination at a ratio of 2:1 demonstrated the best performance. OIT can be used as a simple indicator for a rapid screening of antioxidants for WPC production.
2. The addition of antioxidants can greatly reduce BFPC weight loss and color change after 900 h of thermal weathering. The treated samples only became slightly darker, redder, and yellower while the control samples faded significantly. BFPCs treated with antioxidants only showed small or insignificant color change and weight loss.
3. The MOR and MOE of BFPCs treated with various combinations of antioxidants only decreased slightly or even increased compared to the control samples. The retention ratios of MOR and MOE of BFPCs with antioxidants after thermal weathering were significantly higher than that of the control samples.
4. The addition of antioxidants had a positive effect on the thermo-oxidative degradation resistance of BFPCs. In this case, the optimal parameters were the antioxidant combination of 1076 and DLTP mixed at the ratio of 2:1 with the total concentration prepared at 0.2 wt %.

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