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Improving thermo-oxidative degradation resistance of bamboo fiber reinforced polymer composites with antioxidants. Part II: Effect on other select properties

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ABSTRACT: The first of this two-article study showed that the addition of antioxidants can significantly improve the thermo-oxidative resistance of bamboo fiber reinforced polypropylene composites (BFPCs). In this article, the effect of antioxidants on water absorption, thermal stability, crystallinity, and the dynamic mechanical properties of the composites were investigated. The results showed that the addition of antioxidants resulted in a slight increase in water absorption, but this increase can be reduced by controlling the ratio of the primary and secondary antioxidants. The glass transition temperature (T_g) of composites also slightly increased. However, the effects of antioxidants on the crystallinity as well as other thermal properties of BFPCs were small or even insignificant. The different combinations, ratios, and the adding amounts of antioxidants show tiny differences for all these properties. As a whole, the addition of minor antioxidants in the bamboo fiber (BF) polymer composites will not produce obvious negative effects on their overall performances. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 44199.

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INTRODUCTION

Natural fiber reinforced polymer composites (NFRPC) are attracting global attention and being increasingly used as a wood or plastic replacement in many applications.[1] The major advantages of these composites include acceptable mechanical properties, low cost, and environmental impact, recyclability, and simple maintenance.[2] Many natural fibers such as kenaf, jute, sisal, flax, hemp, and wood fibers have been used as reinforcements in the production of NFRPCs.[3] Bamboo fibers (BFs), with its remarkable mechanical properties and rapid growth, have also been increasingly used as reinforcements of NFRPCs over the past decades.[4]

To-date, studies on NFRPCs have mainly focused on interphase modification because of the inherently low compatibility between the hydrophilic lignocellulosic fibers and non-polar polyolefin plastics. More recently, it has been observed that NFRPCs undergo serious aesthetic deterioration and loss of mechanical strength when exposed to prolonged natural or accelerated weathering.[5] Several methods have been proposed to increase the weathering resistance of NFRPCs, such as improving interfacial properties,[6,7] adding pigments,[8] and applying UV stabilizers.[9,10]

Antioxidants are well-known for its ability to efficiently inhibit oxidation and degradation reactions in plastics.[11] Several categories of antioxidants are available on the market, such as phenolic antioxidants (Irganox 1010, Irganox 1076, Irganox 1330, and BHT)[12,13] and hindered amine light stabilizers (HALSs).[14,15] This study is split into two article: the first article demonstrated that the addition of antioxidants can significantly improve the thermo-oxidative resistance of bamboo fiber plastic polypropylene composites (BFPCs). This study forms the second article and assesses the effects of antioxidants on other select properties of BFPCs that are fundamental to its application. The results of both studies will provide more comprehensive insight on the correlation between antioxidants and BFPC performances.

EXPERIMENTAL

Materials

Industrial bamboo fibers (BFs) with 100 meshes were obtained from Hubei Sanmu Wood Technology Co., Ltd (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 Co., Ltd (China). The densities of PP and MAPP were 0.91 g/cm^3 and 0.90 g/cm^3, respectively. The melting points of PP and MAPP were 161 °C and 156 °C, respectively. For MAPP, the grafting percentage was 1%. Two primary antioxidants: Irganox 1010 [pentaerythrityl-tetrakis-(3,5-di-*tert*-butyl-4-hydroxyphenyl propionate)] and Irganox 1076 [*n*-octadecyl-β-(4-hydroxy-3,5-di-*tert*-butyl-phenyl propionate)], and two secondary antioxidants: Irgafos 168 [Tns-(2,4-di-*tert*-butyl)-phosphite] and dilaurylthiodipropionate (DLTP) were purchased from Beijing Additives Institute (China).

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 and thickness of 3.5 mm (3895, CARVER Co., Ltd, USA). The weight ratio of BFs to PP powder was maintained 45/55 (wt %) and MAPP at 6 wt % (based on PP matrix). The formulations used here are the same as in Part I of this study.

Water Absorption Test

Water absorption (WA) and thickness swelling (TS) were determined according to ASTM D 570. Six specimens (80 mm × 20 mm × 3.5 mm) of each formulation were selected and dried in an oven for 6 h at 103 ± 2 °C. The weight and thickness of the dried specimens were measured to a precision of 0.001 g and 0.001 mm, respectively. The specimens were then placed in distilled water and kept at room temperature for 24 h. Subsequently, the specimens were taken out of the water, surface dried with absorbent paper and re-measured. The values of water absorption in percentage (WA, %) were calculated using the following equation:

$$\mathrm{WA}=\frac{W_1-W_0}{W_0}\times 100 \tag{1}$$

where W_0 and W_1 are the respective weight values of the specimen before and after immersion in water.

The thickness was determined at three marked positions for each specimen and measurements were taken for all six specimens, i.e., the mean values were calculated from 18 points. The thickness of swelling (TS, %) was measured according to the formula:

$$\mathrm{TS}=\frac{T_1-T_0}{T_0}\times 100 \tag{2}$$

where T_0 and T_1 are the respective thickness values of the specimen before and after immersion in water.

Scanning Electron Microscopy (SEM)

The surface morphology of BFPC cross sections was observed with a high-resolution field emission gun scanning electron microscope (XL30-FEG-SEM, FEI, Hillsboro, OR, USA) (operated at 10 kV). The samples were coated with platinum by ion sputtering.

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was performed with a TGA instrument (TA Q 500, TA Instruments, USA). Composite samples weighing between 8–12 mg were scanned from 35 °C to 600 °C at a rate of 10 °C min^{-1} under a constant flow of nitrogen at 40 mL min^{-1}. Three analyses were repeated for each specimen.

Differential Scanning Calorimetry (DSC)

The non-isothermal crystallization behavior of the composite samples was investigated using a TA Q 100 device (TA Instruments, USA) using differential scanning calorimetry (DSC). Samples of 3–5 mg in weight were used for each run with three replicates for each formulation. The samples were heated at 10 °C min^{-1} from 25 °C to 200 °C and held for 5 min in 200 °C to eliminate any thermal history. Samples were then cooled to 25 °C and heated again to 200 °C at the same rate. The degree of crystallinity (X_c, %) was determined from the first cooling and second heating. The degree of crystallinity (X_c, %) was calculated according to eq. (3):

$$X_c=\frac{\Delta H_m}{\Delta H_f W}\times 100 \tag{3}$$

where ΔH_f is the theoretical enthalpy value for a 100% crystalline isotactic PP homopolymer (209 J g^{-1}),[16] and W is the weight fraction of PP in the composites (53 wt %).

Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis (DMA) was performed on the BFPCs under dual cantilever mode using the TA Instrument DMA Q 800 (TA Instruments, USA). The samples (64 mm × 14 mm × 3.5 mm) were tested under a constant deformation amplitude of 15 μm at a frequency of 1 Hz and heating range from −50 °C to 150 °C at a rate of 2 °C min^{-1} under nitrogen atmosphere. Three specimens for each composite type were tested.

Statistical Analyses

To determine the effect of the combinations and ratios of antioxidants on the water absorption, thermal properties, crystallinity, and viscoelastic 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 antioxidant content on BFPCs was conducted on a one-sample ANOVA with the same α significance value. All statistical analyses were performed using PASW Statistics 18.

RESULTS AND DISCUSSION

Effect of Antioxidants on Water Absorption (WA) and Thickness Swelling (TS)

The absorption of water can cause dimensional changes and mechanical degradation in BFPCs. WA and TS are the most widely used indicators for describing the hydrophilicity and dimensional stability of NFRPCs. The effects of adding different antioxidants on WA and TS are presented in Figure 1. The WA and TS of BFPC without any antioxidant treatment were 1.56% and 0.75%, respectively. In most cases, the WA and TS increased slightly with the application of antioxidants. Significant increase in WA and TS were observed for the addition of the 2:1 1010 and DLTP antioxidant combination and the 2:1 1076 and DLTP combination ($p<0.01$, two-way ANOVA) [Figure 1(A)]. Decreasing the ratio of primary antioxidants reduced the WA and TS significantly in these two cases. Figure 1(B) shows that the WA and TS of BFPCs with different contents of antioxidants

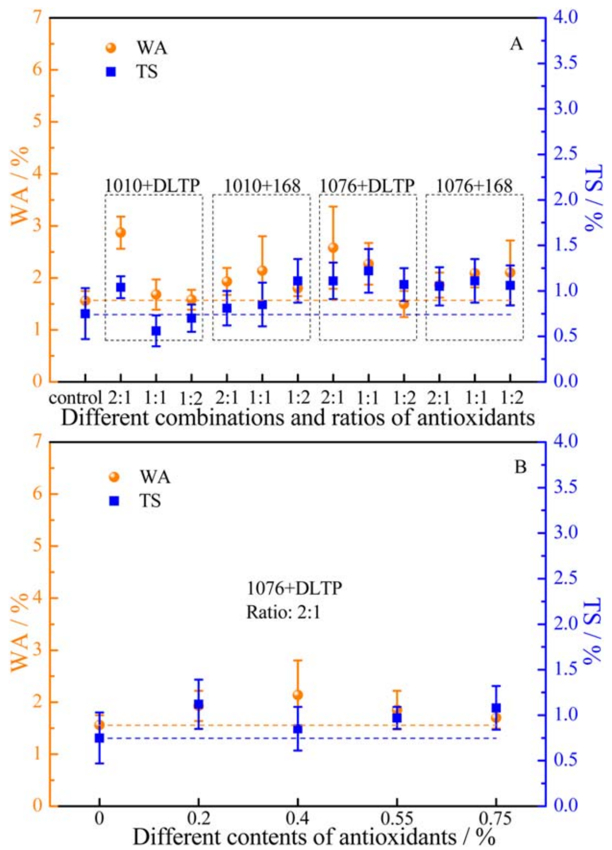

Figure 1. The effect of different combinations and ratios (A), and contents (B) of antioxidants on the water absorption and thickness swelling of BFPCs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

were higher than the control samples, with an average increase of 22.40% and 21.30%, respectively. Meanwhile, varying the contents of antioxidants has little effect on the WA and TS ($p_{WA} = 0.31 > 0.05$, $p_{TS} = 0.51 > 0.05$, one-way ANOVA).

Certain studies in the past presented comparable data in WA and TS for several kinds of NFRPCs. Kazemi Najifi *et al.*[17] reported that the WA and TS of 24 h of wood flour (38 wt %)/PP composites were 4.20% and 2.60%, respectively. Gregorova *et al.*[18] measured the WA of wood (30 wt %)/poly(lactic acid) composites at 5.60%. Furthermore, Altum *et al.*[19] and Wang and Ying[20] found the WA of natural filler (40 wt %) reinforced polymer composites [such as wood flour and BF] to be 4% and 1.70%, respectively.

The hydrophilic BF is mainly responsible for water absorption in BFPCs. The hygroscopicity of lignocellulosic materials is highly correlated with the accessibility of their hydroxyl groups. Water molecules are attached to the hydroxyl groups of bamboo polymers through hydrogen bonding. It is the available hydroxyl groups in the hemicellulose that make it the main polymer in bamboo responsible for moisture absorption.[21,22] Another factor of water absorption may be the interfacial properties in the BF and PP matrix. The gaps or voids within the BF and PP matrix may favor water absorption, as reported by Lopez-Manchado and Arroyo.[23] Figure 2 demonstrates the small gaps in

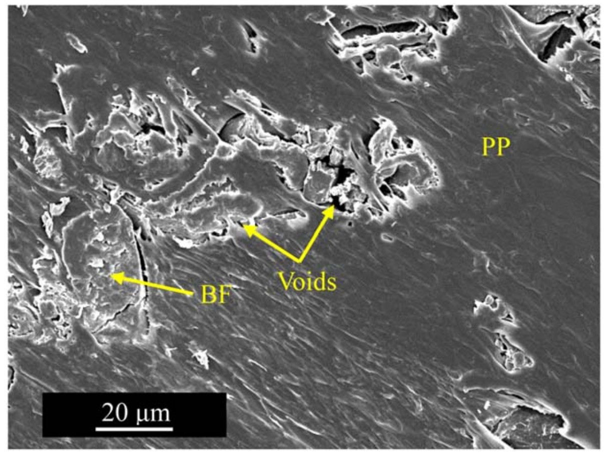

Figure 2. The cross section morphology of BFPC. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the BF and PP matrix, which indicates that BFs were not sufficiently encapsulated by PP, resulting in spaces available for water penetration.

Effect of Antioxidants on Thermal Stability

Figure 3 shows the typical TGA and differential thermal gravity (DTG) curves of BFPCs as functions of temperature. The effects of different combinations, ratios, and contents of antioxidants on the rates of weight loss and characteristic peak temperatures are summarized in Figures 4 and 5. The results highlighted that the

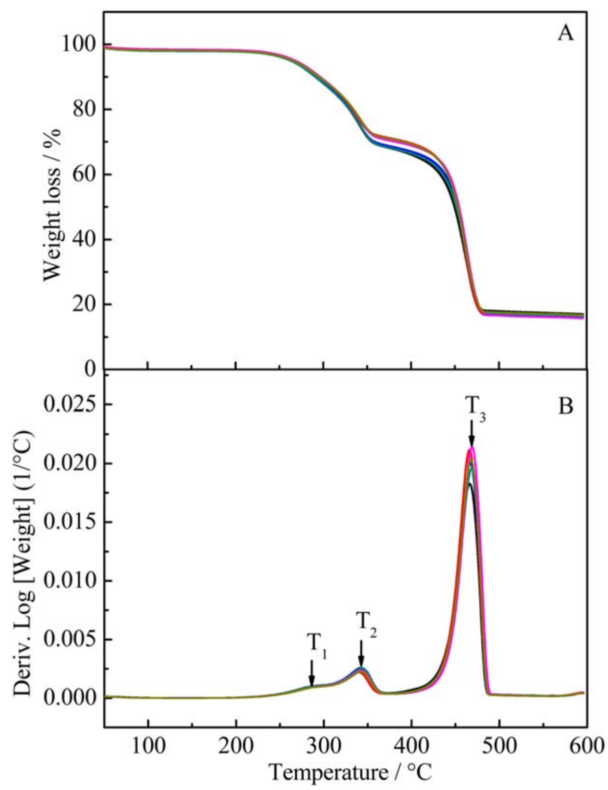

Figure 3. The typical TGA (A) and DTG (B) curves of BFPCs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

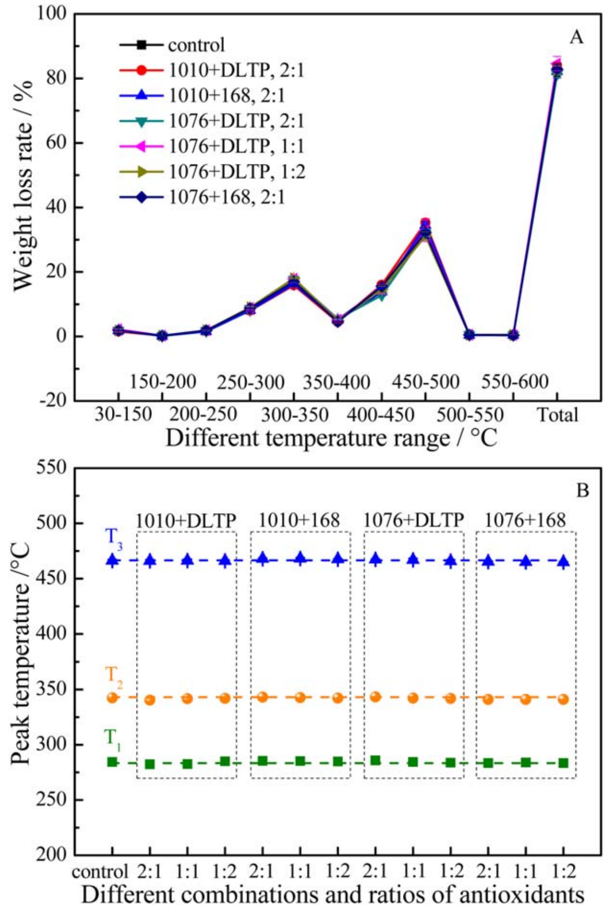

Figure 4. The effect of different combinations and ratios of antioxidants on the thermal parameters of BFPCs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

varying combinations, ratios, and contents of antioxidants have an insignificant effect on the thermal stability of BFPCs, mainly due to the low content of antioxidant in the composites.

The rate of weight loss in the temperature range of 30–200 °C was as low as 3–4%, mainly due to the volatilization of moisture, CO_2, and non-combustible materials.[24] The thermal degradation of BFPCs occurred over three distinct stages [Figure 3(B)]: from 200 to 300 °C with the maximum rate of thermal degradation (peak temperature, T_1) at 283 °C, corresponding to the degradation of hemicelluloses; from 300 to 400 °C with the rate of weight loss at approximately 21% and T_2 at 340 °C, corresponding to the decomposition and disintegration of the glycosidic linkage of cellulose, interunit linkages and condensation of aromatic rings during the pyrolytic degradation of lignin;[25] and from 400 to 500 °C, the most intensive stage of thermal degradation, with the rate of weight loss at approximately 49% and T_3 at 465 °C, corresponding to the degradation of PP and some lignin. Kim *et al.*[26] observed that the degradation of hemicelluloses, lignin, and cellulose occurs between 180 and 350 °C, 250 and 500 °C, and 275 and 350 °C, respectively. The PP matrix is more thermally stable than BFs, with thermal degradation occurring in one stage beginning at about 400 °C and with the maximum rate at 457 °C.[27] Normally, degradation/depolymerization takes place at the weak sites of the PP chain.[28] The results of this study showed that BFPCs have a higher decomposition temperature compared to the neat PP (as indicated by T_3). The addition of BFs can shift decomposition to a higher temperature possibly due to the increased crystallinity of the PP matrix. The same trend was also found in other NFRPCs, such as MFC reinforced PP composites.[27]

Effect of Antioxidants on Crystallinity

The typical curves of DSC for BPFCs are shown in Figure 6. The exothermic and endothermic peaks in Figure 6 are attributed only to the PP matrix in the composites, while the heat response from BF polymers is nearly negligible at this temperature range. The melting temperature (T_m) and crystallization temperature (T_c) of the BPFCs were around 163 °C and 121 °C, respectively. The addition of different antioxidants resulted in little variation on both T_m and T_c.

The crystallinity (X_c) of BFPCs with different combinations, ratios, and contents of antioxidants is summarized in Figure 7. The X_c of the control samples was 43.18%. Comparable values were reported by other studies. For example, Panaitescu *et al.*[2] found that the X_c of treated or untreated hemp fiber (30 wt %)/PP composites ranged from 32.80 to 36.50%. The difference was mainly attributed to the different heterogeneous nucleation abilities of different natural fiber reinforcements. An antioxidant

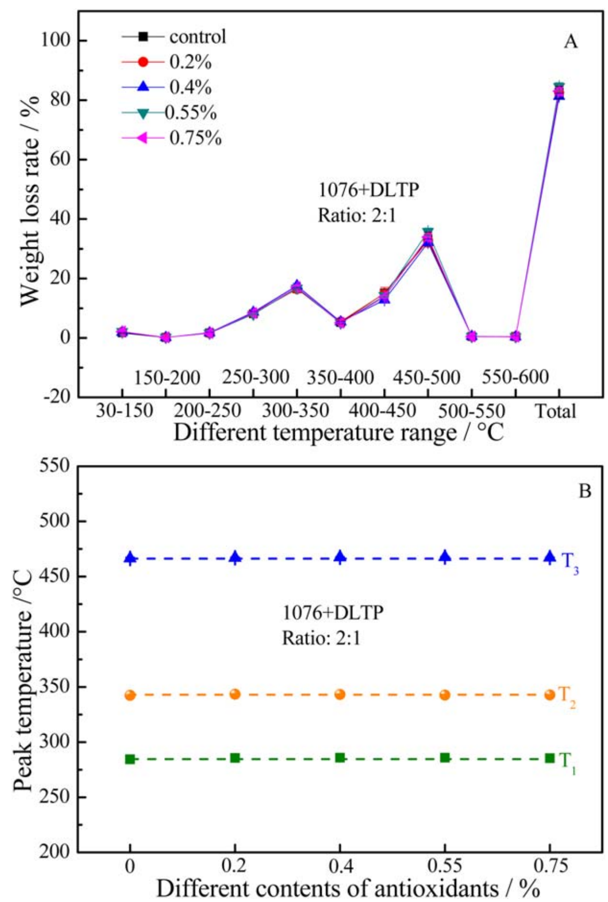

Figure 5. The effect of different contents of antioxidants on the thermal parameters of BFPCs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

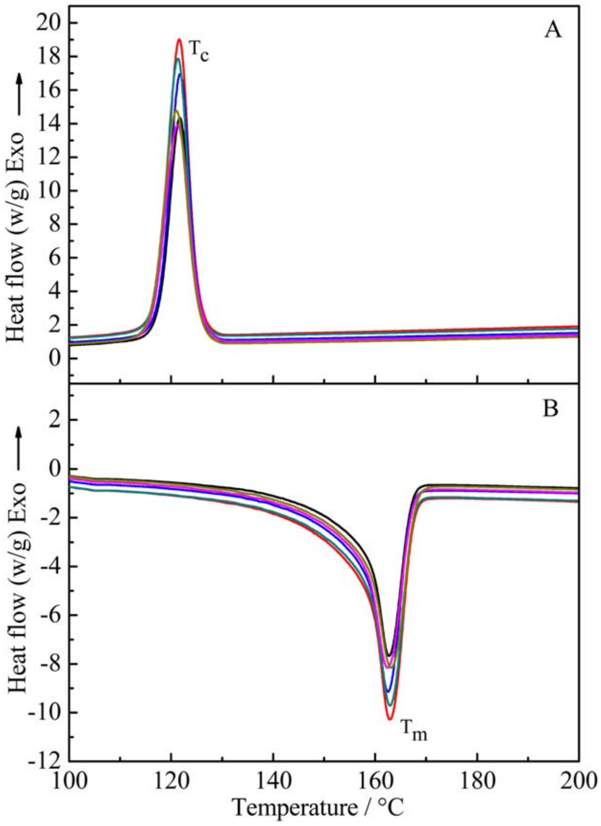

Figure 6. The typical DSC curves of BFPCs during the cooling step (A) and the second heating step (B). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

combination with a high ratio of the primary antioxidant 1010 can slightly increase the X_c by approximately 6%, whereas X_c values decreased with the application of 1076, especially by the largest decline of 15.40% for the combination of 1076 and DLTP at the ratio at 1:2. The X_c of composites prepared with the 168 antioxidant was lower than that with DLTP of similar concentrations, mainly due to the bulk aromatic ring structure of 168, which can embed bulky structures between polymer PP chains and consequently hinder polymer crystallization. Moreover, the X_c declined by an average of 8% with increasing the contents of antioxidant. Therefore, the addition of antioxidants seems to have a slightly negative effect on the crystallization of the PP matrix in the composites. This is partly due to the behavior of antioxidants in acting as a chain accelerator during the semi-crystallization of the PP matrix, such as poly(ethylene glycol) (PEG) in the poly(L-lactic acid) (PLLA) polymer, which can remarkably decrease the density of PLLA spherulites and thus lead to a decline in crystallinity.[29]

Effect of Antioxidants on Dynamic Mechanical Properties

DMA measurements were performed to investigate the dynamic mechanical properties of BPFCs with different antioxidants. Figure 8 exhibits the storage modulus and damping factor (tan δ) of BFPCs as the function of temperature. Dynamic storage modulus represents the inherent stiffness of the material while the damping factor shows the amount of energy dissipated as heat during deformation. With increasing temperature, the storage modulus of BFPCs decreased due to the increased chain mobility of both the bamboo cell wall polymeric components and the PP matrix.[30] Two major relaxations are shown in Figure 8(B). The first was seen at around 8 °C, which was related to the β-relaxation of the PP chain. The β-relaxation is a glass-rubber relaxation of amorphous fraction and the maximum peak was assigned to the glass transition temperature (T_g).[31] The second minor and broad relaxation was seen in the range of 70–85 °C, which corresponds to the superimposed α-relaxation of the PP matrix and BFs. Boyd[31] reported that the α-relaxation is the glass-rubber relaxation of the amorphous fraction in the presence of the crystal phase in the PP matrix. Moreover, the α-relaxation was also related to the applied fibers. Geethamma *et al.*[32] reported that the obvious α-relaxation for short coir fiber-reinforced natural rubber composites occurred at around 50–75 °C. Ye *et al.*[33] found that there was no significant α-relaxation in polar fiber/PP composites, and that the same results were also found in pine fiber/PP composites[22] and jute fiber/PP composites.[34]

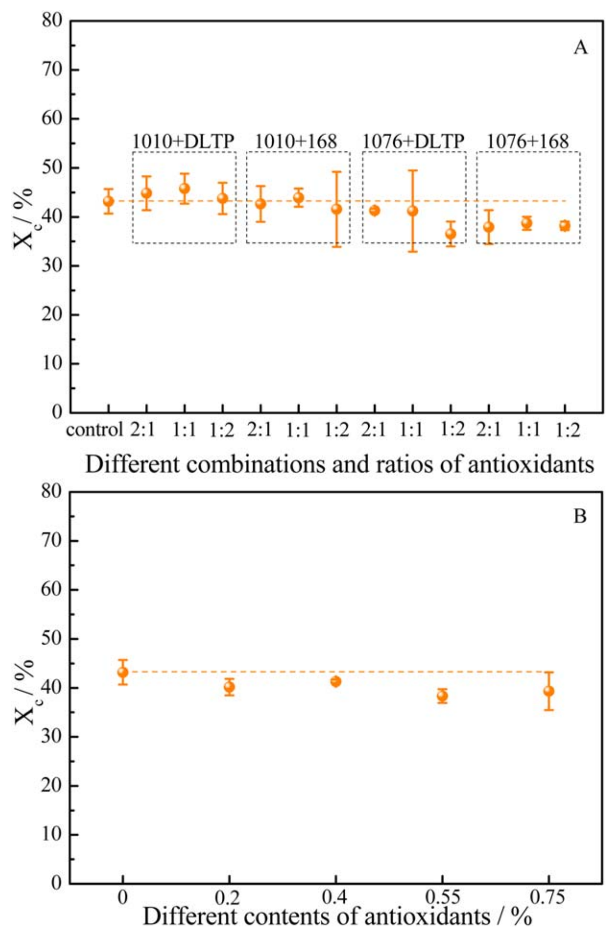

Figure 7. The effect of different combinations and ratios (A), and contents (B) of antioxidants on the crystallinity (X_c) of BFPCs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

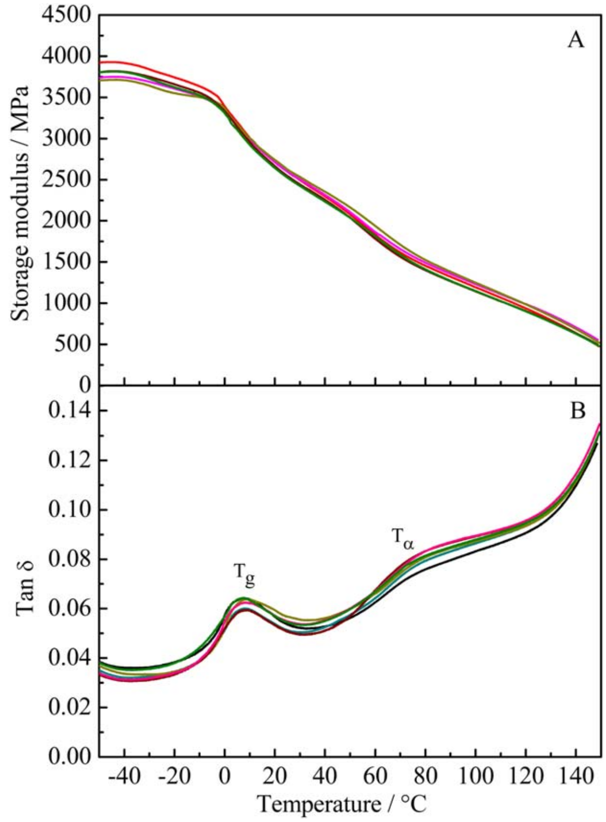

Figure 8. The typical storage modulus (A) and damping factor (tan δ) (B) curves of BFPCs. (Note: T_g and T_α indicate the temperature of β-relaxation and α-relaxation). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The storage modulus and tan δ values of the BFPCs at 20 °C are presented in Figure 9. The storage modulus of the BFPCs with different combinations and rations of antioxidants ranged from 2.46 to 2.79 GPa, and the tan δ values varied between 0.05–0.06, respectively. The storage modulus of the BFPCs with the primary antioxidant 1010 was higher than the composites containing the 1076, except for the combination of 1076 and 168 with the ratio of 1:2. This mainly attributed to the higher molecular weight of 1010, which led to the higher strength. Moreover, the tan δ values of BFPCs almost decreased with the application of antioxidants and the values of composites containing the primary antioxidant 1076 were normally higher than the composites with 1010. It was noted that higher tan δ values indicated poorer interfacial bonding.[35–37] Therefore, the interfacial bonding between bamboo fibers and the PP matrix containing 1010 was better than that with 1076, which is favorable for stress transfer and consequently the storage modulus. Moreover, the result for the storage modulus was in agreement with X_c, where a higher X_c value led to a larger storage modulus. Meanwhile, two significant decreases were observed for the combination of 1076 and 168 with the ratio of 2:1 and 1:2 ($p < 0.01$, two-way ANOVA). Figure 9(B) shows that the storage modulus and tan δ decreased slightly and the different contents of antioxidants have insignificant effect on these factors ($p_{\text{storage modulus}} = 0.471 > 0.05$; $p_{\tan\delta} = 0.805 > 0.05$). Comparable results were reported by Hosseinaei *et al.*[22] They found that the storage modulus and tan δ of a pine (50 wt %)/PP composite were 4.36 GPa and 0.06, respectively. This can be ascribed to the mechanical limitation posed by the higher fiber content embedded in the viscoelastic matrix, thereby reducing the mobility and deformation of the matrix with increasing temperatures.[38]

The peak temperature of β-relaxation (T_g) and α-relaxation (T_α) of BFPCs are presented in Figure 10. The values of T_g slightly increased except for the combination of 1010 and DLTP with the ratios of 2:1 and 1:1, and the highest improvement by 36.20% for the combination of 1076 and 168 with the ratio of 1:1 [Figure 10(A)]. This discrepancy was likely due to the different compatibilities between antioxidants and the PP matrix. Furthermore, the values of T_α decreased slightly with the addition of antioxidants, likely due to the decline in crystallinity. Three obvious increases were also observed for the antioxidant combinations of 1010 and DLTP (1:1 ratio), 1076 + DLTP (1:2 ratio), and 1076 + 1687 (1:1 ratio). Figure 10(B) reveals that the values of T_g for BFPCs increased first and then decreased with an increasing content of antioxidant. Meanwhile, the values of T_a generally decreased with an increase in antioxidant content, where the highest decline was at 11% at the antioxidant content of 0.75 wt %.

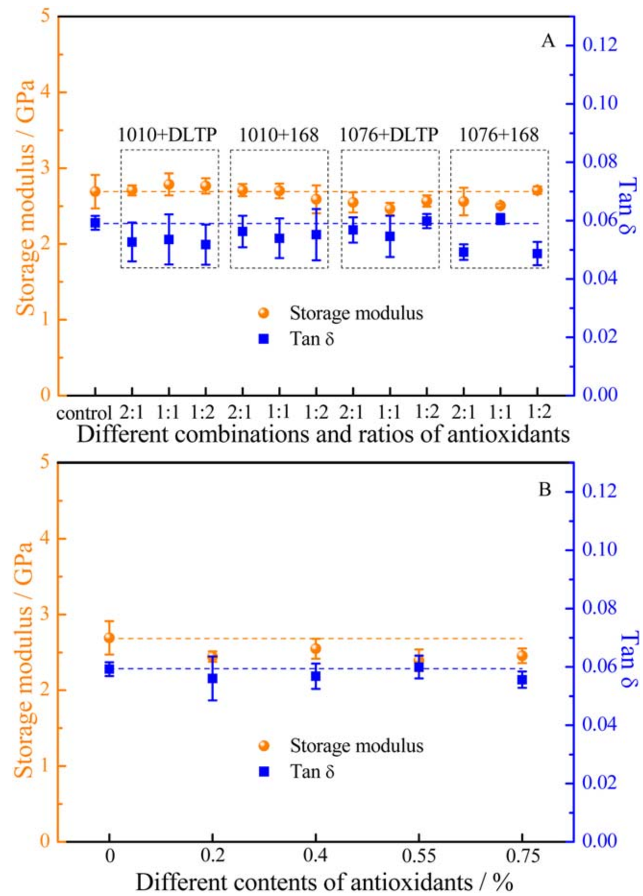

Figure 9. The effect of different combinations and ratios (A), and contents (B) of antioxidants on the storage modulus and tan δ values of BFPCs at 20 °C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

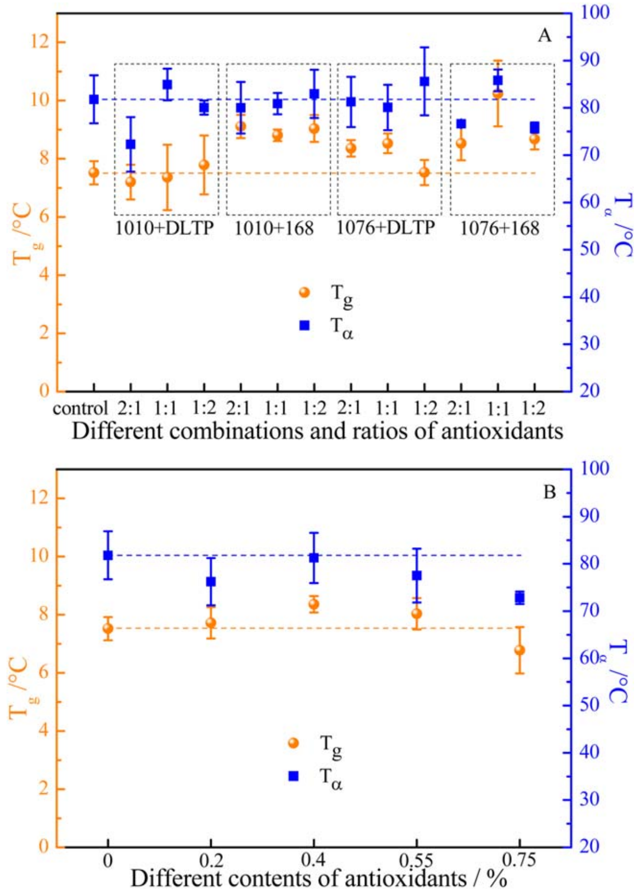

Figure 10. The effect of different combinations and ratios (A), and contents (B) of antioxidants on the T_g and T_α of BFPCs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSIONS

The effects of antioxidants on water absorption, thermal stability, crystallinity, and the dynamic mechanical properties of bamboo fiber/polypropylene composites (BFPC) were studied. The results led to the following conclusions:

1. BFPC water absorption and thickness swelling increased slightly with the addition of some antioxidant, ranging from 1.50–2.87% and 0.56–1.22%, respectively. This increase, however, can be reduced by controlling the ratio between the primary and secondary antioxidants.
2. The combinations, ratios, and contents of antioxidants have little effect on the thermal stability of BFPCs. The addition of antioxidants seems to have a slightly negative effect on the crystallization of the PP matrix in the composites.
3. The storage modulus and tan δ of BFPCs normally decreased with the application of antioxidants. The T_g of BFPCs slightly increased after the addition of antioxidants while T_α was less affected.
4. As a whole, the addition of minor antioxidants in natural fiber polymer composites will not produce obvious negative effects on their performance.

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