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Boron-Based Mildew Preventive and Ultraviolet Absorbent Modification of Waterborne Polyurethane Coatings on Laminated Bamboo

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Abstract: In order to improve the outdoor exposure performance of laminated bamboo, boric acid/borax and UV absorbents, including triazole (UV1130), nano–TiO_2, and nano–SiO_2, were used to modify waterborne polyurethane (WPU) coatings, respectively. The physical and chemical properties of the coatings with and without modification were evaluated by adhesion strength, contact angle, wear, and temperature-resistance experiments. The antimildew properties of the coatings were evaluated by the bacteriostatic zone method, and the pyrolysis characteristics were investigated through TG–FTIR analysis. The results showed that, when compared with the unmodified WPU coating, the coatings with different modifications had stronger wear resistance; the mass loss of the best C4 coating was only 0.0078 g, which was 0.0203 g less than that of the unmodified C0 coating. However, when compared to the unmodified coating, the wettability of the modified coating increased to different degrees, and the contact angle of the C4 coating with the most obvious effect was only 36.50°. During the curing process of the modified coatings, the UV absorbents and boric acid/borax would interact with the C–N, C–O, and C=O bonds in the coating and change the molecular structure of the WPU. The thermal stability of the coatings with different modifications was enhanced. The best result, a 76.27% weight loss, was observed in the modified coating with boric acid/borax and 1.0% nano–TiO_2. Different modified coatings had a certain degree of control effect on Aspergillus Niger, and the reason for this was considered the combined effect of boric acid/borax and UV absorbents.

Keywords: waterborne polyurethane (WPU); laminated bamboo; coating; antimildew; UV absorbent

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1. Introduction

Bamboo is a kind of natural biomass material that has been widely used in furniture, paper making, textiles, and buildings for its fast growth rate, high strength, good toughness, easy processing, large output, etc. [1,2]. However, the first challenge for bamboo-based materials is that the rich nutrients, such as starch, protein, sugar, and fat, that are observed in bamboo [3] make bamboo prone to mold attacks by fungus and insects [4], causing serious adverse effects on the use value and economic value of bamboo and bamboo-based products. One of the traditional and widely used methods to improve its biological resistance was to introduce antimildew preservatives into bamboo [5–8]. Among them, the boron-based antimildew preservatives have been proven to protect bamboo against many different molds, such as Aspergillus Niger, Trichoderma Viride, Penicillium Citrinum, etc. Han et al. used inorganic reagent copper sulfate, boric acid, and hydrogen peroxide to carry out antimildew and bacteriostatic experiments and found that the inorganic reagent with the concentration of 1% copper sulfate, 1.5% boric acid, and 6% hydrogen peroxide had a better bacteriostatic effect, and the control effect on poplar and bamboo was 100%

for 17 days [9]. The Aspergillus Niger and Trichoderma Viride mildew fungi could be prevented by sol−gel coating with a Si−Al−Cu−P antimildew agent [10]. Although boron-based antimildew preservatives have many advantages, such as a rich resource, lower price, mammal safety, and higher efficiency, their wide application has long been disturbed by extremely higher leaching loss when used in outdoor exposure areas [11].

Another challenge for bamboo application is poor weathering resistance, and one of the main reasons for this is attributed to the photodegradation of ultraviolet radiation when used outside. Photodegradation resistance treatment methods can be divided into two categories: surface finishing and bamboo modification treatment [12]. Surface finishing modification involves a coating with added photodegradation resistance additives, and the main types of these additives are ultraviolet absorbents and light stabilizers. Queant et al. showed that the clear acrylic water-based coating formulation added with commercial ultraviolet absorbents (UVAs), hindered amine light stabilizers (HALS), or poly (methyl methacrylate) (PMMA) microspheres, saw that the color change of the samples was minimized and the production of photo-oxidation compounds in the binder was also limited [13]. Organic absorbents have been proven to decompose more quickly than inorganic ones during outdoor exposure [14], although organic absorbents have been proven to be more conducive to improving the color stabilization of bamboo, especially for a coating with benzotriazole modifications. Many kinds of inorganic particles, such as nano–ZnO, nano–TiO_2, nano–Fe_2O_3, and nano–Al_2O_3, were selected as UV absorbents because of their quantum size and could produce a "blue shift" effect to shield UV light effectively [15]. Al_2O_3–ZnO–Y_2O_3 modified coatings have been proven to improve the ultraviolet radiation resistance of the coating, which was due to the large extinction coefficient of the ZnO and Y_2O_3 materials in the ultraviolet band [16]. Can et al. showed a positive synergistic effect of benzotriazole organic ultraviolet absorbents and micron and nanometer TiO_2 particles on coating properties, such as hardening, strengthening, and toughening, and this also had a very significant "ultraviolet shielding" effect and absorbed photons irradiated by ultraviolet light [17]. Some research showed that hybrid coatings performed better than TiO_2 coatings in protecting fibers from UV, and UV1130 especially reinforced the UV–protective ability of the TiO_2 coating because of its strong UV absorbance among the hybrid coatings obtained, and Tinuvin® 477 and Tinuvin® 123 (Nanjing Pinning Coupling Agent Co., Ltd., Nanjing, China) exhibited excellent synergistic effects when used together with UV1130 and improved the UV-protective ability of the resultant hybrid coatings [18].

The present study aims to reinforce the mildew resistance and anti-ultraviolet aging abilities of laminated bamboo when used in outdoor exposure. The environmental WPU coating modified with boric acid/borax and UV1130, nano–TiO_2, or nano–SiO_2 was finished on the surface of laminated bamboo and was evaluated for its coating properties, wettability, antimildew performance, and thermal stability. The research results will be conducive to providing useful information for the industrial design of producing more seasonable schedules for bamboo-based products that are used outdoors.

2. Materials and Methods

2.1. Modifications of Waterborne Polyurethane Coatings

Based on the preliminary research results [19,20], boric acid/borax (mass ratio of 1:1) with excellent antibiological capabilities and flame-retardant performance was selected as the antimildew additive and was added to WPU coatings at three different ratios (boric acid/borax:WPU = 1:1, 1:1.5, and 1:2). As the adhesion of the coating is particularly important to protecting laminated bamboo from damage, the seasonable ratio between boric acid/borax and WPU was determined by the adhesion performance according to GB/T 4893.4—2013 [21].

Based on the test results above, ultraviolet absorbents, including UV1130, nano–SiO_2, and nano–TiO_2 with different mass fractions (1.0%, 2.0%, and 3.0%), were added into the antimildew-modified WPU coatingsto determine the best UV resistance modification conditions. According to different UV absorbers and their addition above, the samples were defined as C0-C9, as shown in Table 1. The C0 was the blank control group among them.

Table 1. Different UV absorbents modifications.

Specimens	Antimildew Preventive	UV Absorbents	UV Absorbents Addition (wt%)
C0	—	—	—
C1 C2 C3	Boric acid/borax	UV1130	1.0 2.0 3.0
C4 C5 C6		nano–TiO_2	1.0 2.0 3.0
C7 C8 C9		nano–SiO_2	1.0 2.0 3.0

2.2. Laminated Bamboo Surface Finishing

The modified WPU coating was applied with a brush on the surface of the laminated bamboo (100 mm × 100 mm, 110 mm × 50 mm, and 50 mm × 20 mm). Each layer of coating was painted with 2 g of WPU, and the coating was composed of four layers. It should be noted that the layer was dried completely before the next layer of coating was added. Then, all the specimens were painted (Table 1) and placed in air drying conditions for 7 days to ensure that the coating was completely dry.

2.3. Physical and Chemical Properties of Coatings

After air drying, the physical and chemical properties of the coatings on the laminated bamboo were evaluated according to GB/T 4893.4-2013 [21], and three replicates were taken in each condition. For the adhesion crosscutting determination, six groups of lines perpendicular to each other were drawn on the surface of the coatings with a multiedge tool, and three places on the surface were randomly selected as the test locations. After drawing, a tape about 30.00 cm in length was pasted on these lines and quickly torn off to observe the drop failure of the coatings, and we evaluated the coating adhesion ratings according to the criteria, as Table 2 illustrates (GB/T 4893.4-2013) [21]. The samples with better adhesion capabilities were selected to perform the following experiments.

Table 2. Evaluation criteria of coating adhesion rating.

Rating	Evaluation Criteria
0	Cut edge completely smooth, without any drop failure
1	Drop failure of small flakes of the coating at the intersections of the cuts. A crosscut area is not distinctly greater than 5%.
2	The affected crosscut area is distinctly greater than 5% but not distinctly greater than 15% is affected.
3	The affected crosscut area is greater than 15% but not significantly greater than 35%.
4	Large pieces or some squares are partially or completely peeling off, and the affected cross area is obviously greater than 35% but not significantly greater than 65%.
5	The drop failure exceeds the fourth rating.

For the wear resistance measurement, the specimens were rubbing at a speed of 60 rpm, and the total test revolutions = 1000 r under gravity of about 500 g. Then, the surface of the coatings was swept off with a soft brush, and the mass after rubbing was recorded. The average weight loss was more than 0.03 g, which is unqualified according to GB/T 4893.8-2013 [22].

For the cold resistance and heat temperature difference measurement, the specimens were placed in a constant temperature and humidity box (40 °C; 95% relative humidity) for 1 h and then taken out immediately and put into the refrigerator (−20 °C) for 1 h. This experiment cycle was repeated 3 times and evaluated the change of the coatings according to GB/T4893.7-2013 [23]. The coating surface in the middle part of the specimens was observed with a quadruple magnifying glass. If any of the defects, such as cracks, bubbles, the obvious loss of gloss, or discoloration, was observed in the specimens, they would be assessed as unqualified.

2.4. Bacteriostatic Test Method

Aspergillus Niger (International Centre for Bamboo and Rattan, Beijing, China) was used as a template for the bacteriostatic bacteria. The sterilized culture medium was cooled to 50 °C and then poured into the plate. The bacterial solution was diluted 10–fold to obtain bacterial suspensions by gradual dilution. The standardized density of the bacterial suspension was 2 × 108 CFU/mL (colony-forming units per milliliter). After the agar plate was solidified, the bacterial suspension (500 μL) was sucked into the solid medium for coating. A coating rod was utilized to spread the bacterial solution evenly on the plate [24]. The WPU coating and modified WPU coatings with three replicates were placed on the agar medium, respectively, with the sterile forceps so that the coating and the medium were in intimate contact. The bacterial reproduction could be observed thereafter and photographed to record the size of the bacteriostatic zone.

2.5. Static Contact Angle Test

The surface contact angle was measured with a VAC20 (Angstrom Sun Technologies Inc., Boston, MA, USA) contact angle measuring instrument. After sucking a certain amount of ultraclean water with a syringe, it was ensured that there were no air bubbles in the syringe, and a syringe was installed on the contact angle measuring instrument. The samples were placed on the loading table to ensure that the focal length and the position of the samples were adjusted clearly and properly. A total of 20 points per second was recorded, and three samples in each group were repeated to process the data with the VCA20 software to obtain the coating contact angle change diagram and the final contact angle value.

2.6. Fourier Transform Infrared Spectrometer (FTIR) Determination

The coatings were naturally dried on a square glass plate, and the samples were detected by Nicolet 6700 Fourier Transform Infrared Spectrometer produced by Thermo Electron Corporation, Madison, WI, USA. About 2 mg of the sample was weighed and mixed with about 160 mg of KBr powder and then ground into fine powder in an agate mortar many times, dried, and pressed into tablets. Finally, the tableted samples were put into the sample chamber, and the iD1 mode was used to scan 16 times with a resolution of 4 cm^{-1}, and the test scan range was 4000–500 cm^{-1}.

2.7. Thermogravimetric Analysis (TG)

In this experiment, the thermogravimetric analysis of the coatings was carried out by using the Q500 thermogravimetric analyzer produced by TA Instruments (Shanghai, China). Each sample was prepared at about 10 mg and heated at a rate of 20 °C/min in a nitrogen atmosphere. The tested temperature range was 0 °C to 800 °C to explore the classification temperature and the corresponding mass loss.

3. Results and Discussion

3.1. Analysis of the Physical and Chemical Properties of Coatings

3.1.1. Coating Adhesion Analysis

The adhesion grade of the coatings on the laminated bamboo is shown in Table 3, in which the ratios of boric acid/borax to WPU were set at 1:1, 1:1.5, and 1:2, respectively. It showed that when the ratios of boric acid/borax to WPU were 1:1 and 1:1.5, the adhesion grades were reduced to grade 2, and a small amount of coating failure could be observed during the coating-cutting process. In contrast, for the coating with a ratio of 1:2, the adhesion grade was almost the same as the WPU coating without modification, and both of them could keep at Grade 1. The result was possibly attributed to the negative effect of a higher ratio of boric acid/borax in the WPU coating, which would reduce the viscosity of WPU and lead to the internal stress distributed unevenly [25–27]. Considering the practical application cost of the WPU coatings, the ratio of boric acid/borax to WPU was set as 1:1 in the following experiments.

Table 3. Adhesion grades of the coatings with different ratios between boric acid/borax and WPU.

Antimildew Agent	Antimildew Agent:WPU	Adhesion Rating
-	0:1	1
Boric acid/borax	1:1	2
Boric acid/borax	1:1.5	2
Boric acid/borax	1:2	1

The adhesion grades of the coating with different weathering modifications are shown in Table 4. These show that, except for UV1130 (2.0% and 3.0%), all of the other UV absorbent modifications improved the adhesion of the modified waterborne polyurethane coatings, and the adhesion grades were all up to Grade 1. It seemed that a higher UV1130 played a negative effect on the adhesion resistance of the modified WPU coatings, which is consistent with the research of Chang [28]. According to his study, phase separation was not obvious in the microstructure of the benzotriazole UV absorber composites with low contents, while phase separation occurred at higher contents. The reason is the weakness of the stress connection between the molecular chains of the polyurethane matrix due to the presence of hydrogen bonding within the benzotriazoles/polyurethane composites and the hybridization of small organic molecules in the polyurethane matrix. In addition, Yu found that the addition of UV1130 could effectively delay the yellowing phenomenon and yellowing rate after the aging of the paint film, weakening the color change of the paint film to a certain extent, but too much addition would lead to an increase in color change [29]. The samples with better adhesion resistance and lower UV absorbents (C1, C4, and C7) were selected as the test specimens for the following experiments. C1, C4, and C7 were respectively added with 1.0% of different types of ultraviolet absorbents (UV1130, nano–TiO_2, and nano–SiO_2), and C0 (without any modification) was used as the control group.

Table 4. Adhesion grades of the coatings with different weathering modifications.

Test Number	Antimildew Agent Composition	UV Absorbent-Composition	UV Absorbent Addition (wt%)	Adhesion Grade
C0	-	-	-	2
C1	Boric acid/borax	UV1130	1.0	1
C2	Boric acid/borax	UV1130	2.0	2
C3	Boric acid/borax	UV1130	3.0	2
C4	Boric acid/borax	nano–TiO_2	1.0	1
C5	Boric acid/borax	nano–TiO_2	2.0	1
C6	Boric acid/borax	nano–TiO_2	3.0	1

Table 4. *Cont.*

Test Number	Antimildew Agent Composition	UV Absorbent-Composition	UV Absorbent Addition (wt%)	Adhesion Grade
C7	Boric acid/borax	nano–SiO_2	1.0	1
C8	Boric acid/borax	nano–SiO_2	2.0	1
C9	Boric acid/borax	nano–SiO_2	3.0	1

3.1.2. Wear Resistance Analysis

As can be seen from Figure 1, when compared to C0, in which the mass loss was 0.0281 g, the mass losses in the C1, C4, and C7 groups were reduced to 0.0172 g, 0.0078 g, and 0.0168 g, respectively. The better wear resistance of the modified coatings was attributed to the additives (especially the nanoparticles) in the coatings, which promoted the formation of a denser and stronger network structure in the coating. Sun et al. observed a similar result, where nano–boron carbide could enhance the physical and chemical properties of the WPU coatings [30].

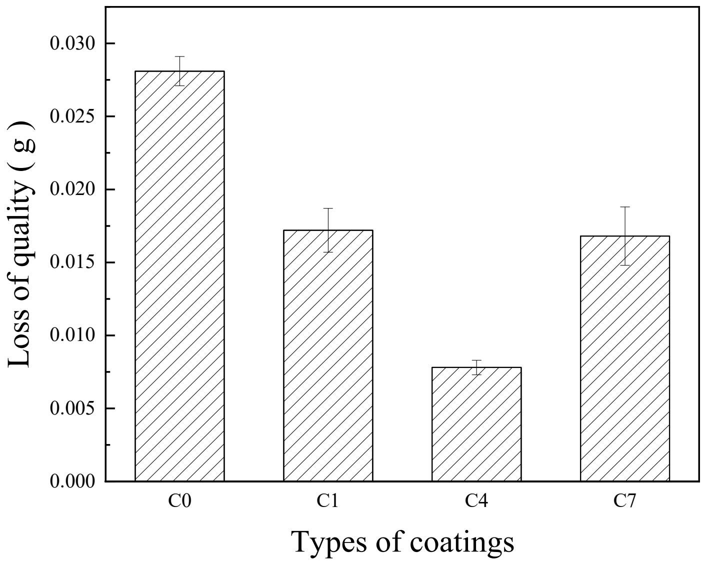

Figure 1. Mass loss of WPU-modified coatings after wear resistance test.

3.1.3. Temperature Resistance Analysis

After three cycles of low- and high-temperature/relative humidity treatments, the specimens in the groups C0, C1, C4, and C7 were not observed to have any obvious chalking, cracking, bubbling, loss of gloss, or discoloration in the coatings, which indicated that the addition of the antimildew agent and ultraviolet light absorbents in the modified coating did not impair the better cold and temperature resistance of WPU coating.

3.2. Antimildew Performance Evaluation

As shown in Figure 2, the specimens in group C0 were thoroughly permeated with mycelium, which demonstrated that the WPU coating itself had no antimildew effect on Aspergillus Niger. In contrast, the modified coatings, including C1, C4, and C7, showed obvious bacteriostatic circles, and the average sizes of the bacteriostatic zones were up to 9.53 mm, 8.43 mm, and 7.17 mm, respectively. Although boric acid/borax was an effective antimildew agent, which has been proven by many researchers [9,31–34], the leaching performance was still one of the most intractable issues, especially for its outdoor application. In this study, boric acid/borax was introduced into the WPU coating, which was conducive to impeding the leaching process and providing long-term antimildew protection for laminated bamboo. Many researchers have proven that UV1130, nano–TiO_2, and nano–SiO_2 have an antimildew effect on Aspergillus Niger [35–37], which was also proved in our study, and it seemed UV1130 had better performance than the others.

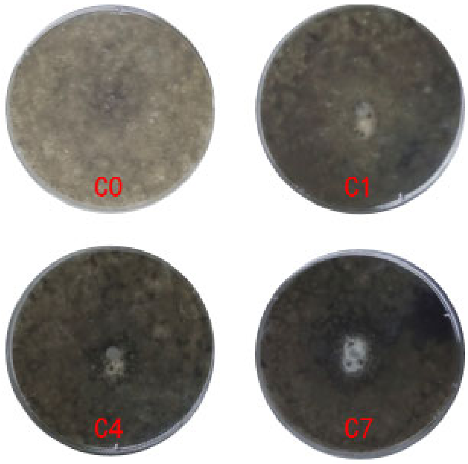

Figure 2. The real effect of antimildew of each coating.

3.3. Wettability of Coating

As shown in Figure 3, the contact angle of the unmodified WPU (C0) was 97.40°, while the contact angles of the modified coatings (C1, C4, and C7) decreased to 73.50°, 36.50°, 87.00°, respectively. The result was mainly due to the addition of boric acid/borax with strong hygroscopicity [38–40], and the types of UV absorbents were the reason for the difference of coating wettability, in which the coating modified with nano–SiO_2 had the lowest wettability [41–43].

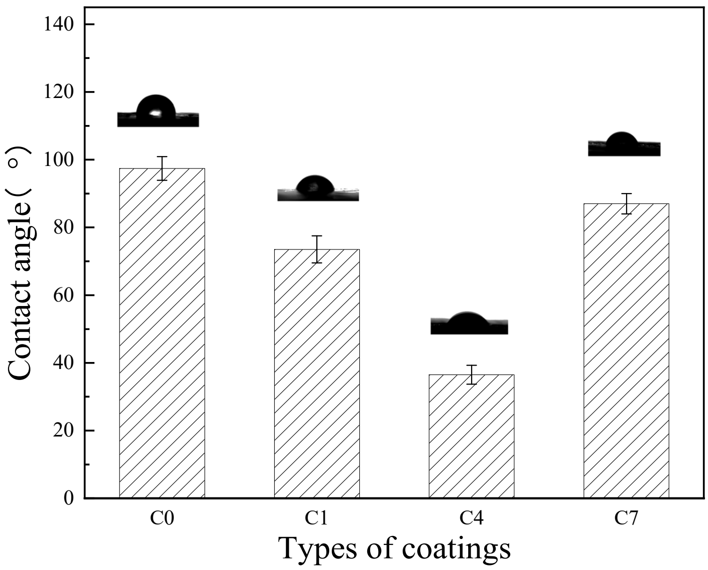

Figure 3. Contact angle of the coatings with and without modifications.

3.4. FTIR Analysis

The results of the FTIR spectra taken from the WPU coatings with or without modifications in the range of 4000–500 cm^{-1} are displayed in Figure 4. All of these coatings had a weak broad peak at 3376.7 cm^{-1}, which should be the N–H stretching vibration in the amide bond group –NHCOO– in the urea group [44] and a notable increase in the intensities in the coatings modified by nano–SiO_2 or nano–TiO_2 ultraviolet absorbent was observed. The result indicates that the nanoparticles had dispersed into the WPU coating during the drying process, which led to more N–H stretching vibrations. Two broad peaks with low intensities at 2932.7 cm^{-1} and 2872.7 cm^{-1} are associated with the symmetric and antisymmetric stretching vibrations of methylene $–CH_2$ on the main polymer chain [45], and these were observed clearly in the samples of the C0 group, but weakened (C1) or disappeared (C4, C7) in the modified coatings, possibly due to the addition of the ultraviolet light absorbents, reacting with these functional groups during outdoor exposure. This result was similar to some existing studies [46,47], in which TiO_2 and SiO_2 promote redox reactions under the condition of photocatalysis and construct C–C bonds through intermolecular formation. The strong absorption peak at 1720 cm^{-1} is the stretching vibration of C=O in the ester group –COO– contained in the polyurethane [48], the concave peak around 1670.7 cm^{-1} belongs to the C=O of urea bonded to one NH group of a nearby urea moiety [49], 1143.5 cm^{-1} is the stretching vibration peak of polyester C–O–C bonds [50], and 1050.7 cm–1 belongs to the N–CO–O symmetry stretching vibration [51]. When compared with the unmodified WPU coating (C0), the absorption peaks of the modified coatings (C1, C2, and C3) were all obviously weakened, which indicated that the ultraviolet absorbents could interact with the C–N, C–O, and C=O bonds in the coating in the curing process, resulting in the change of spectral peak intensity.

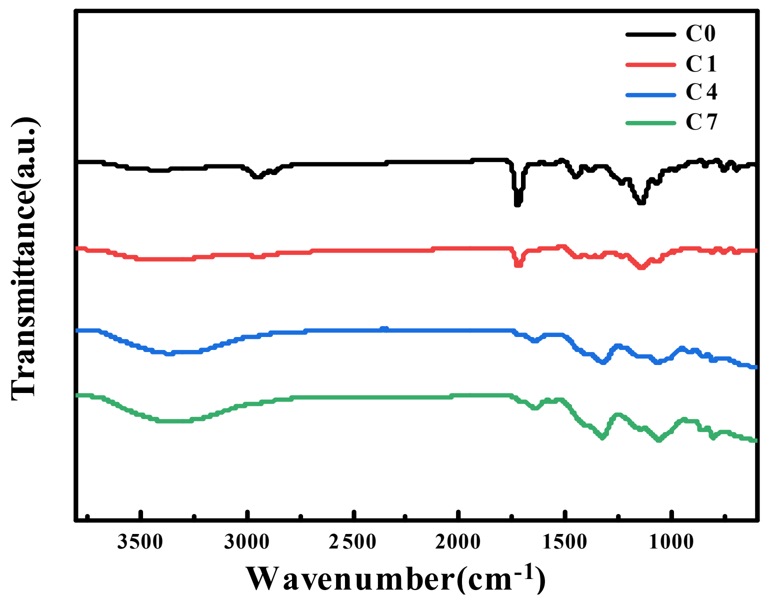

Figure 4. Infrared spectrum of coatings with and without modifications.

3.5. Thermal Stability Performance Analysis

The thermal stability performance of the four WPU coatings with and without modifications was tested by a thermogravimetric analyzer; the TG and the DTG profiles obtained under an inert atmosphere are shown in Figure 5. From the TG profiles, different modifications had obvious effects on the hydrolysis process of the coatings, and the weight loss of C0 was the highest at 77.17%, while the losses of C1, C4, and C7 were 72.81%, 67.27%, and 68.93%, respectively. The reason might be attributed to the boric acid/borax contained in C1, C4, and C7, which had better flame-retardant capabilities and could form a glass-like coating film covered on the surface of the coatings to block the entrance of oxygen and heat at higher temperatures [52–54]. Moreover, some researchers have proven that UV absorbents, including nano–SiO_2, nano–TiO_2, and UV1130, could effectively reduce the pyrolysis of coatings [55–57]. Among them, C4 had the best stability, because the network-like nano–TiO_2 covering the surface of the carbon layer enhanced the thermal stability of the coating. According to the DTG profiles, there are three obvious weight loss rate peaks for the four coating samples. The first peak appeared around 120 °C, which we attributed to the evaporation of water and moisture in the coatings [58,59], and for which the peak of C4 was the most obvious, maybe because nano–TiO_2 is prone to changing the pyrolysis process of WPU coatings at lower pyrolysis temperatures. The second peak showing T around 270 °C was not obvious in all coatings and is attributed to the beginning of the movement of hard segment molecular chains, such as the decomposition of –CH_3 and –COOH in WPU coatings. The third peak appeared around 400 °C, in which the pyrolysis rate of each sample reached the highest and was mainly caused by the breakage of the functional groups, such as –RNHCOOR′ and –$CO(NH_2)_2$ in the WPU coatings. After 480 °C, the coatings had basically pyrolyzed completely.

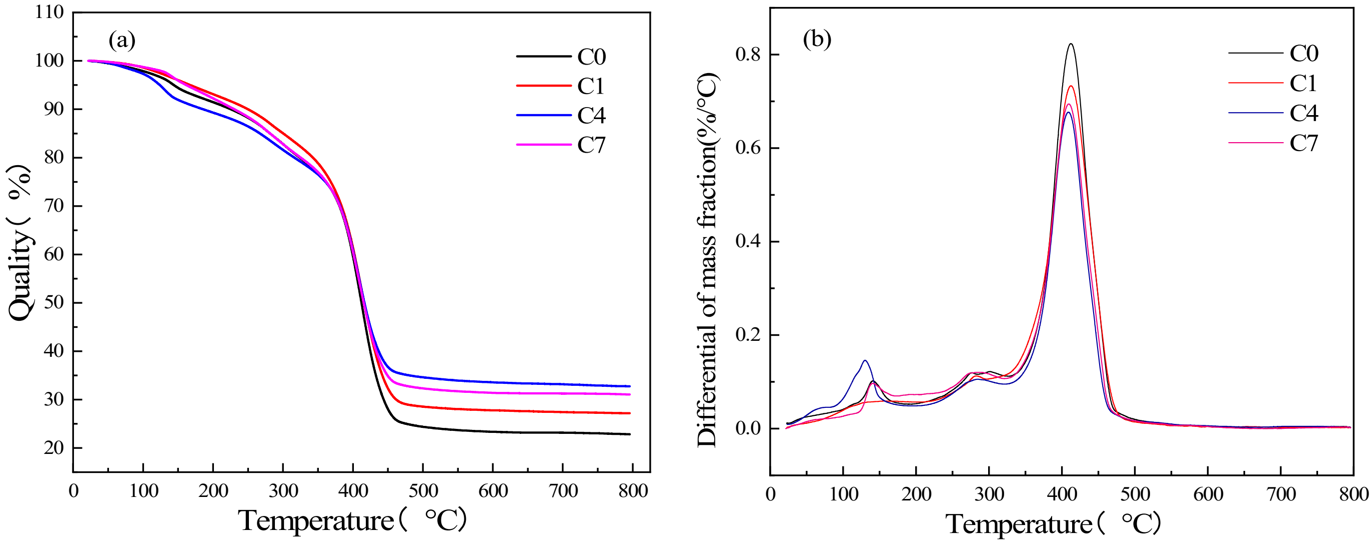

Figure 5. (**a**) The TG profiles of the four WPU coatings with and without modifications under inert atmosphere. (**b**) The DTG profiles of the four WPU coatings with and without modifications under inert atmosphere.

4. Conclusions

In this work, boric acid/borax and three UV absorbers (UV1130, nano–TiO_2, nano–SiO_2) were used to modify waterborne polyurethane coatings, and the protective performance of bamboo laminates was verified. The results show that the addition of nanoparticles improved the wear resistance but did not affect the temperature resistance. All three UV absorbers had an antimold effect, among which UV1130 had the better performance. Besides, the addition of boric acid/borax improved wettability to varying degrees. According to TG analysis, the thermal stability of the modified WPU coatings was effectively improved. This research demonstrates a facile approach to enhancing the outdoor protection performance of bamboo products, which lays a foundation for the further industrial application of low-cost bamboo products in the future.

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