

Photodegradation and Photostability of Bamboo: Recent Advances

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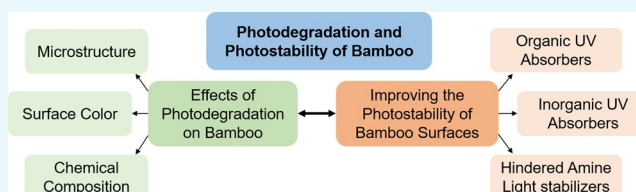
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ABSTRACT: Bamboo and its products are widely used in indoor and outdoor fields. Photodegradation occurs easily on the surface when bamboo is exposed to ultraviolet (UV) light from solar radiation. This induces surface discoloration and degrades the physical properties of bamboo, which not only negatively affects its utility and aesthetic characteristics but also restricts its application in outdoor environments. In this work, we review the mechanism of bamboo photodegradation, in which the behavior of lignin is key. The changes in bamboo's microstructure, surface color, and chemical composition during photodegradation are described in detail. Methods for enhancing its photostability, including the application of transparent coatings containing UV absorbers and hindered amine light stabilizer compounds on bamboo surfaces, are then systematically summarized, and potential approaches to combat the photodegradation of bamboo surfaces are discussed. On the basis of the recent advances of photodegradation and photostability of bamboo, this review provides new insights into the scientific application and protection of bamboo in the outdoor field.



1. INTRODUCTION

Humans have long used bamboo in various environments and applications. Bamboo is a biomass material that is rapidly renewable, biodegradable, and useful for land rehabilitation and carbon sequestration. Owing to its advantages such as high strength-to-weight ratio and easy processing techniques, bamboo is widely used as a building material, as a decorative material for making handicrafts, and in other applications. Furthermore, it is attracting increasing attention because of its superior performance in various applications and its ability to address top-quality timber supply issues. The development and utilization of abundant bamboo resources could gradually replace some large-diameter and precious wood materials in furniture, construction, and building applications; this is of practical significance for overcoming the conflict between the increasing demand for wood and the need to protect forest resources.

However, under combined exposure to external elements over time, bamboo is continually subjected to photodegradation and photooxidation, resulting in surface degradation.¹ The factors that affect the bamboo surface are solar radiation (including UV, visible, and infrared light), moisture (dew, rain, snow, and humidity), temperature, and oxygen. Most damage to the bamboo surface is induced by light energy from solar radiation, which causes a wide range of photochemical changes. Similar to wood, bamboo is mainly composed of cellulose (~55%), hemicellulose (~20%), and lignin (~25%), all of which absorb UV light to different extents. UV light only accounts for ~6.8% of solar radiation; however, owing to its high energy, it can destroy many

chemical bonds in the main components of bamboo, especially lignin. For example, the critical UV wavelengths required to break C–C, C–O, and C–H single bonds are 346, 334, and 289 nm, respectively. Additionally, fungi can invade the bamboo interior, potentially accelerating mildew growth and decay.² The photodegradation of bamboo reduces its market acceptance and also degrades the utility and service life of bamboo products. Therefore, studying the photodegradation mechanism is important for increasing the light stability of bamboo surfaces, prolonging the service life of bamboo products, reducing the product maintenance period, and widening the field of potential bamboo applications.

Previous research on photodegradation focused on wood and its associated products. Because the composition of wood and bamboo is very similar, the results of the study on wood photodegradation also apply to bamboo to a large extent. In this work, we review the latest research on bamboo photodegradation, describe the observed changes in the microstructure, surface color, and chemical composition of bamboo during the photodegradation process, discuss the photodegradation mechanism of bamboo, summarize the enhancement effect of various transparent coatings on bamboo surface photostability, and explore future research trends in

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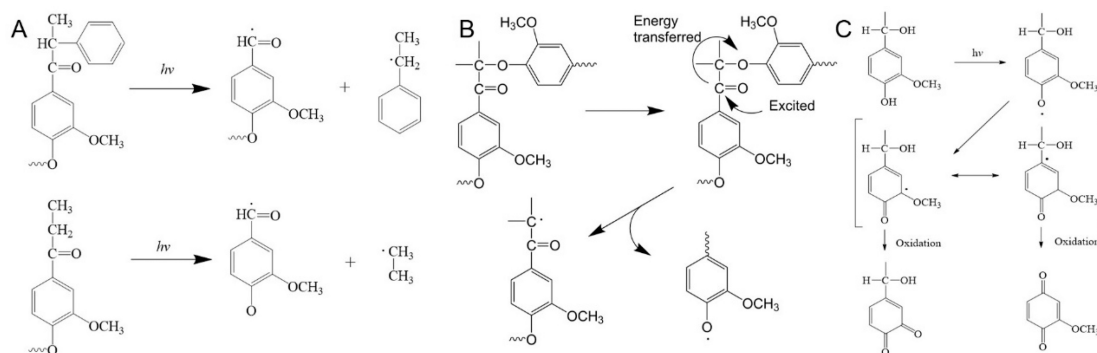


Figure 1. Photochemical reactions of lignin. (A) Norris type-I photoreaction. (B) Dissociation of the β -aryl ether linkage in lignin by an energy-transfer process via excited α -carbonyl group. (C) Formation of *o*- and *p*-quinonoid structures during UV irradiation of lignin. Adapted with permission from ref 7. Copyright 2000 Marcel Dekker, Inc.

this field. This review will provide a reference for the increasing market acceptance and commercial value of bamboo products for outdoor use.

2. EFFECTS OF PHOTODEGRADATION ON BAMBOO

2.1. Microstructure. After xenon arc light irradiation for 160 h, the parenchyma cells of Moso bamboo (*Phyllostachys edulis*) were observed to be slightly deformed. Cracks formed on the cell walls, but the structures of the cell corners and intercellular layers were essentially intact.¹ After 8 weeks of UV light irradiation, fine cracks and different degrees of damage were observed in Moso bamboo near the parenchyma cells in the tangential section, near the pits in the inner wall of the xylem vessels, and in the intercellular spaces of the fiber cells.³ After natural aging for 1 year, more V-shaped cracks were observed on the outer surface of 2–3 year old Moso bamboo than on that of 1 year old Moso bamboo.² Bamboo cross-sections showed severe damage to basic structures, with cracks extending beyond 8–10 cells beneath the surface to the vascular bundle boundary with an erosion depth of 5–8 cells (100–150 μm); the presence of fungal spores was also noted.² Thus, photodegradation not only destroys the bamboo material but also accelerates mildew growth and subsequent decay.

2.2. Surface Color. After aging, the surface color of the bamboo typically darkens and transforms toward red and yellow, and the total color difference (ΔE) increases. During an accelerated aging process using illumination from a xenon lamp, the ΔE of Moso bamboo gradually increased to 15.58 after irradiation for 160 h, whereas the ΔE values of two woods were already above 20 under the same conditions.⁴ After UV-accelerated aging, the ΔE of Moso bamboo increased with aging time and ΔE was close to 25 after 672 h.⁵ During the natural aging process, the brightness of bamboo gradually decreased, and ΔE increased rapidly in the first 28 days and then decreased slightly to reach 15.23 after 112 days.⁶ Furthermore, the color changes in 1–3 year old Moso bamboo were similar. The value of ΔE also increased rapidly in the first 3 months of natural aging, whereas there was little change over 3–6 months. After 12 months, ΔE decreased to approximately 20.² The change in bamboo color was a result of photochemical reactions of its chemical components triggered by environmental stimuli: the main source of discoloration is the quinoid structure formed by the photochemical reaction of light-sensitive lignin in bamboo, including red water-insoluble *o*-quinone and yellow water-soluble *p*-quinone. In the initial

stage of irradiation, the formation of *p*-quinone caused rapid yellowing of the bamboo surface. With the scouring of water and prolonged UV exposure, the lignin content decreased, the cellulose content increased, and the color of the bamboo faded.

2.3. Chemical Composition. The main components of bamboo (cellulose, hemicellulose, lignin, and extractives) absorb UV radiation, but their UV sensitivity depends on their structure. Among these components, lignin was found to be the most sensitive to UV radiation, as 80–95% of the UV light incident on the bamboo surface is absorbed. The lignin absorption peak is centered at a wavelength of 280 nm with a front tail extending to 400 nm.³ Therefore, lignin is considered the most easily photodegradable component in bamboo and wood. Indeed, because of the large number of active groups in lignin and the low binding energy of most carbon–oxygen bonds, the secondary alcohol, hydroxyl, carboxyl, aromatic, and phenolic groups on lignin are prone to form free radicals under UV exposure. The constant generation of free radicals leads to the photodegradation of lignin and is considered the main reason for the photodegradation of bamboo. The lignin photodegradation mechanism was summarized by Hon and Shiraishi⁷ in Figure 1. The C–C bonds adjacent to a α -carbonyl group are photodissociated via a Norris type-I reaction (Figure 1A), resulting in the reduction or elimination of side chains and a decrease in C1 content. The α -carbonyl group can effectively absorb light and achieve an excited state, thereby transferring the light energy to the β -aryl ether bond, resulting in the cleavage of the ether bond to generate phenolic and carbon radicals (Figure 1B). The phenolic hydroxyl groups react with light rapidly to produce phenolic radicals, which are transformed into *o*- and *p*-quinonoid structures by demethylation or cleavage of the side chain (Figure 1C). To date, research on photodegradation has focused on cellulose and lignin, with relatively few studies on hemicellulose.

The overall relative content of lignin decreases after photodegradation, but the degree of reduction in lignin content varies in different parts of the bamboo. For example, after 28 and 56 days of photoaging, the content of lignin in the outer bamboo layer decreased by 6.99 and 11.32%, respectively, whereas the lignin content near the inner bamboo layer decreased by 11.32 and 17.50%, respectively.³ This indicates that the outer layer of bamboo is more resistant to photodegradation than the inner layer; the dense texture of the outer layer makes it difficult for UV light to penetrate the bamboo. Research on the correlation between the wood density and degradation rate showed an approximately linear

Table 1. Light-Stabilization Additives Used in Transparent Coatings

type	system	commercial name	acronym	description	physical properties ^a			
					M_w , g/mol	T_m , °C	D , nm	ref
organic	powder	Tinuvin 326	BTZ	2-(2-hydroxy-3- <i>tert</i> -butyl-5-methylphenyl)-5-chlorobenzotriazole	318.5	138–141		
		Chimassorb 81	BP	2-hydroxy-4-(octyloxy)benzophenone	326.43	48–49		14
		Tinuvin 770	HALS	bis(2,2,6,6-tetramethyl-4-piperidinyl)sebacate	481	81–85		
		Chimassorb 944		poly[6-[(1,1,3,3-tetramethylbutyl)amino]-1,3,5-triazine-2,4-diyl] [(2,2,6,6-tetramethyl-4-piperidinyl)imino]-1,6-hexanediyl [(2,2,6,6-tetramethyl-4-piperidinyl)imino]	2000–3100	100–135		
inorganic	dispersion		TiO ₂	nanosized anatase TiO ₂			10–20	15
			ZnO	nanosized ZnO			30; 20	16

^a M_w , molecular weight; T_m , melting range; D , diameter.

relationship between the two within a density range of 0.3–1.0 g/cm³.⁸ It is difficult for water and light to penetrate high-density wood, and it suffers less photodegradation than lower-density wood.⁷ This explains the large difference between the degradation rates of earlywood and latewood.⁸ Comparing the photodegradation behaviors of bamboo and wood revealed that the rates of lignin degradation and hydroxyl generation for bamboo were lower than those for wood, indicating that bamboo is more resistant to photodegradation.⁹ This is because the content of syringyl (S) units, which are less prone to photodegradation than guaiacyl (G) or *p*-hydroxypropane (H) units, is higher in bamboo lignin than in wood.

Light radiation has been shown to have little effect on cellulose. Indeed, cellulose photodegradation studies have shown that cellulose exposed to UV and visible light irradiation slowly degrades, and some chemical bonds are broken under irradiation at wavelengths > 340 nm.⁷ Irradiation with UV light of wavelength > 280 nm dehydrogenated the C-1 and C-5 positions, while at wavelengths as low as 254 nm, dehydroxylation also occurred in the C-5–C-6 chain of the cellulose side chain. However, the UV radiation in sunlight is mainly distributed in the wavelength range of 290–400 nm, where the content decreases with further decrease in wavelength. Furthermore, the chemical bond energy of cellulose is relatively high, and the poor penetration of UV light makes it difficult to degrade the cellulose crystalline region. Studies have shown that the cellulose crystalline area of bamboo was unaffected by photodegradation after UV-accelerated aging and natural aging,^{2,3} but the relative crystallinity increased by 8.35–16.13% after UV aging for 56 days.³ This may be related to an observed decrease in the cellulose amorphous area and corresponding relative increase in the crystalline area.¹⁰

Hemicellulose also suffers from photodegradation to some extent. Comparing bamboo's nuclear magnetic resonance spectra before and after natural aging for 1 year, the relative intensities of hemicellulose (21 ppm) and carboxyl carbon (173 ppm) peaks decreased in the aged samples indicating that the lignin–hemicellulose matrix was first destroyed during natural aging.² Another study used Fourier transform infrared spectroscopy to analyze the changes in the surface groups of wood after UV-accelerated aging revealed that, although hemicellulose could be degraded, the wood damage caused by photodegradation after the application of a surface coating was not obvious.¹⁰

The extractive contents of bamboo are relatively low; the content of phenyl alcohol extractive is 4.29–6.47%, and the main chemical components of bamboo are esters, ketones, and alcohols. Extractives play an important role—second only to that of lignin—in the photodegradation of bamboo. Currently, there are different views on the effects of extractives on the photodegradation rate. A study of wood phenolic extractives found that, in the early stage of accelerated aging by a xenon lamp, the presence of extractives enhanced the photochromic and surface delignification.¹¹ However, another study determined that after accelerated UV aging for 384 h, extractives protected lignin against UV degradation because unsaturated phenols preferentially absorb UV light.¹² The observed photodegradation of wood after heat treatment was also consistent with this observation.¹³

3. MECHANISM OF BAMBOO PHOTODEGRADATION

The UV photodegradation of lignin is initiated by the formation of free radicals, possibly owing to the oxidation of phenolic hydroxyl groups. Free radicals rapidly interact with oxygen molecules to generate heat-sensitive and photosensitizing hydroperoxide via hydrogen peroxide radical intermediates.⁷ Lignin contains phenolic hydroxyl groups and ether bonds; phenoxy radicals readily generated from phenolic hydroxyl groups are the main intermediates formed in lignin subjected to light irradiation. Phenoxy radicals can be excited by light or react with oxygen to induce the demethylation of the guaiacyl groups in lignin, resulting in the final *o*-quinoid structure, while decreasing the number of aromatic structures and increasing the number of the conjugated carbonyl group. The quinoid structure formed by the photochemical reaction of lignin was found to be the main chromophore group causing the discoloration of wooden materials, while other auxochromic groups included hydroxyl, carboxyl, amino, and ether bonds. Therefore, the color change is considered a suitable metric for monitoring the degradation of lignin.

4. IMPROVING THE PHOTOSTABILITY OF BAMBOO SURFACES

When an aesthetic bamboo surface is required for decorative uses (floors, panels, furniture, etc.), the easiest and most common method for inhibiting the UV light-induced photodegradation of lignin is applying a transparent additive-containing light-stabilization coating to the product surface.

Commonly used light-stabilization additives are listed in Table 1.

4.1. Organic UV Absorbers. Organic UV absorbers include triazine (HPT), benzophenone (BP), and benzotriazole (BTZ), all of which contain hydroxyl groups in their structures. These absorbers convert UV energy into heat energy and form stable hydrogen bonds and hydrogen bond chelate rings that can protect the substrate surface and substrate/coating interface (Figure 2). Although HPT out-

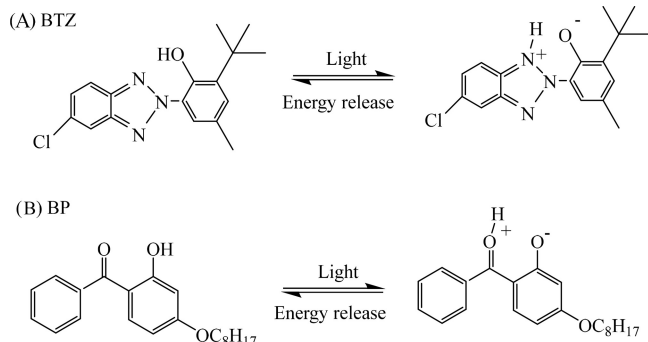


Figure 2. Photostabilization mechanisms of (A) BTZ and (B) BP. Adapted with permission from ref 14. Copyright 2012 Wiley Periodicals, Inc.

performed BTZ in both laboratory and outdoor weathering tests, the range of HPT applications may be limited by its light yellow color. BTZ and BP have two absorption peaks in the UV region and absorb very little visible light, making them more suitable for the preparation of transparent UV-protective coatings (Figure 3).¹⁵ Studies have shown that coatings

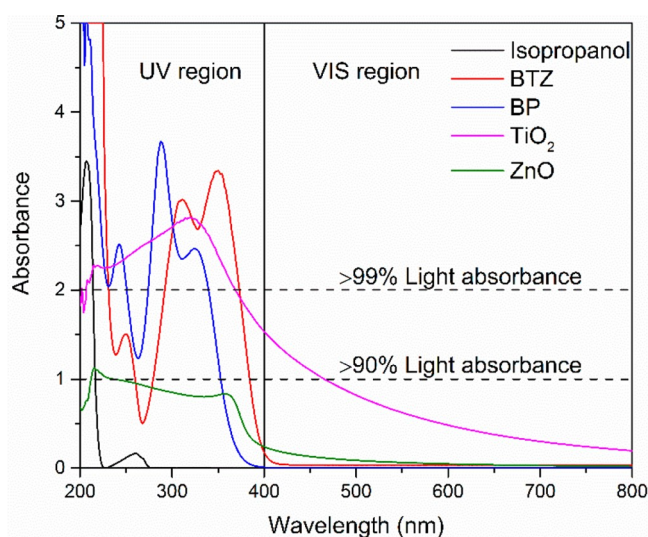


Figure 3. UV-vis spectra of various 0.01 wt % UV absorbers dispersed in isopropanol. Reprinted with permission from ref 15. Copyright 2018 Elsevier B.V.

prepared by compounding BTZ, ethyl acetate, and acrylic resin effectively improved the light stability of bamboo surfaces (Figure 4)⁶ and inhibited the aging and cracking of acrylic resin.¹⁵ The critical additive loading of BTZ was determined to be 1.82 g/m².¹⁷ Acrylic coatings with 3 wt % BTZ and BP effectively protected bamboo from UV-accelerated aging for 380 and 150 h, respectively, and inhibited the photo-

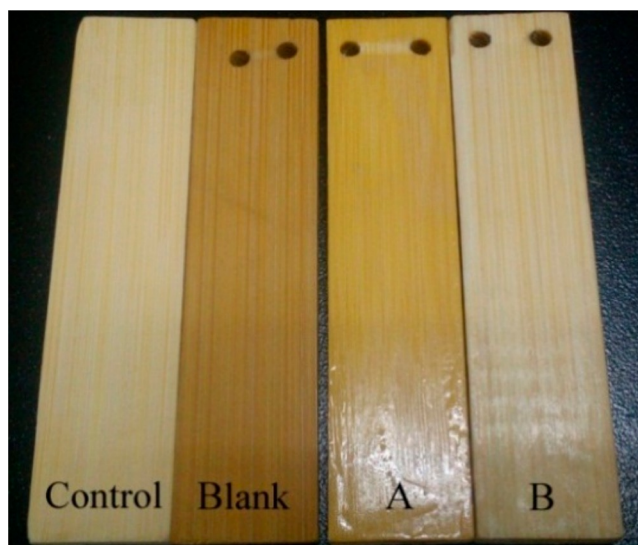


Figure 4. Enhancement of bamboo surface photostability by application of clear coatings containing BTZ: control, original bamboo; blank, bamboo after aging without coating. (A) Bamboo coated without BTZ after aging; (B) bamboo coated with BTZ protection after aging. Adapted with permission from ref 6. Copyright 2015 Editorial Department of *Journal of Nanjing Forestry University*.

degradation of lignin and generation of hydroxyl groups.¹⁵ Furthermore, the UV-blocking effect of BTZ and BP was better than that of two inorganic UV absorbers (ZnO and TiO₂) measured independently at the same concentration. In addition to their excellent UV-shielding properties, organic UV absorbers are lightweight, corrosion-resistant, inexpensive, and easy to prepare. However, their disadvantages include poor heat resistance (for example, the melting point of BP is only 48–49 °C), melting under UV radiation,¹⁵ and an inability to protect lignin from the degradation induced by visible light at wavelengths above 400 nm.

4.2. Inorganic UV Absorbers. Inorganic UV absorbers generally use metal oxide nanoparticles (particle size, 20–50 nm) to absorb or scatter light and can absorb UV and visible light in the wavelength range of 400–500 nm. Because metal oxide nanoparticles do not photodegrade, their protective abilities are considered superior to those of organic UV absorbers in this respect. Inorganic UV absorbers such as ZnO, TiO₂, and Fe₂O₃ have the advantages of stability over long-term aging, high specific surface area, and wide absorption in the UV and visible light regions (Figure 4). The development of nanotechnology has further promoted the widespread application of inorganic UV absorbers in transparent coatings for bamboo and wood materials. Nanoscale ZnO and TiO₂ have become the focus of research owing to their excellent UV-shielding properties and are mainly applied as nanoparticle-based composite coatings or nanoparticle sol additives. A ZnO/polypropylene nanocomposite coating was observed to significantly reduce the degree of photodegradation, and the addition of nano-ZnO improved the ductility and tensile strength of the coating.¹⁸ In addition, the instance of coating cracks during photodegradation was significantly reduced. Weichert et al. prepared ZnO-based acrylate coatings using nano-ZnO prepared in the laboratory and tested the surface properties of the coating after artificial weathering for 1500 h on China Fir wood (*Cunninghamia lanceolata* Hook). The use of nano-ZnO prevented delamination at the substrate-coating

interface, reduced the yellowing of the substrate surface, and improved the hydrophobicity of the substrate as well as the optical properties of the coating.¹⁹ The critical loading of nano-ZnO in the polyurethane–acrylic transparent topcoat was determined to be 2 g/m².²⁰ However, when the protective effect of the coating was more important than its transparency, the thickness loss value, reduction of color deepening, and gloss retention were the most suitable after the addition of 2 wt % nano-ZnO. When the nano-ZnO content increased to 5 wt %, both color deepening and mass loss reached the lowest values observed in the experiment.²¹

The ability of nano-TiO₂ and ZnO to absorb light depends on their bandgap energies ($E_{\text{gap/TiO}_2} = 3.0$ eV; $E_{\text{gap/ZnO}} = 3.2$ eV). They can only absorb light with energy greater than their band gap energy. At the same concentration, nano-TiO₂ has a stronger UV shielding performance than nano-ZnO. The UV light absorption range of nano-TiO₂ is narrower than nano-ZnO, and its UV-shielding performance was found to be slightly worse. In addition, the particle size of nano-TiO₂ had a significant influence on its performance.²² When the TiO₂ particle size was 10 nm, almost no UV light was transmitted and the ΔE after aging was minimal. The performance of 15 nm TiO₂ particles was also better than that of organic UV absorbers, while 20 nm TiO₂ particles had the largest chromatic aberration and UV transmittance. Using a TiO₂ sol of 40–90 nm particles to form a thin film on the surface of bamboo improved its anti-photochromic performance. After aging at 105 °C for 120 h and three loading cycles, ΔE of the modified bamboo was only half that of the control.²³ Notably, this approach can retain the natural appearance of bamboo and effectively improve its antibacterial properties and mildew resistance.²⁴ A comparison between organic (BTZ or BTZ mixed with a hindered-amine light stabilizer (HALS)) and inorganic UV absorbers (10 or 15 nm TiO₂ or transparent nano-Fe₂O₃) as coating additives showed that, under simulated outdoor conditions, the organic UV absorbent coating had a higher ΔE and cracked easily owing to its higher glass transition temperature after aging.²⁵

Despite the promising performance of inorganic UV absorbers, there remain some drawbacks associated with their use as surface additives for outdoor wood materials. First, the dispersion of the nanoparticles has been shown to affect the performance of nanocomposite coatings. In general, nanoparticles can be effectively dispersed and integrated into a polymer system to achieve the desired protective effect on the substrate when they are used as the sole coating additive. Surface modification of the nanoparticles can improve their dispersion in the organic solution to a certain extent, but may reduce their UV-shielding performance. Indeed, the UV and visible light transmittances of nanocomposite coatings prepared by treating 20 nm ZnO with an organic dispersion aid were significantly lower than those prepared using only 20 and 20–60 nm ZnO powders.¹⁶ In addition, some studies have indicated that nanocomposite coatings prepared using nano-ZnO without treatment with a dispersion aid had better photostability. Second, the hydrophobicity of the substrate was enhanced by a surface film formed by the nanoparticle sol loading method. However, the strength of this film was low and it easily lost adhesion and ran off the surface, indicating that it cannot protect the substrate for long periods of time.²⁶ In addition to absorption in the UV region, inorganic nano-oxides can absorb visible light at wavelengths of 400–500 nm

(Figure 4). Lower visible light transmittance values indicate poorer transparency of the coating. In particular, the refractive index of TiO₂ ($n = 2.6$) is higher than that of ZnO ($n = 1.9$), and its light scattering ability was superior. Indeed, the addition of nano-ZnO was found to have only a slight effect on the transparency of coatings.²⁰ Moreover, the high cost of inorganic nanoparticles limits their applications.

The synergistic effects of organic and inorganic UV absorbers has been investigated to optimize the coating, considering their respective advantages and disadvantages. In this recent study, two types of UV absorbers and surfactants were blended with an acrylic resin to prepare coatings.¹⁵ At the same concentration, the coating containing a two-component UV absorber improved the light stability of the bamboo surface to a greater extent than that of coatings containing only one of the UV absorbers. Besides, the combination of the two absorber types alleviated both the agglomeration of inorganic UV absorbers and the self-degradation of organic UV absorbers to a certain extent.

4.3. Hindered Amine Light Stabilizers. Currently, hindered amine light stabilizer (HALS) compounds are considered the most effective light stabilizers for polymer materials. They effectively capture the active free radicals generated by photo-oxidative degradation on the surface of the material to generate stable, nitrogen oxide-free radicals that protect against degradation. Indeed, special monomer HALS derivatives can act as active lignin stabilizers by trapping the free radicals formed on the surface of wood materials. To improve UV absorption and prevent coating degradation, HALS materials have often been applied with organic UV absorbents and antioxidants, among others. It has also been reported that HALS compounds can protect phenol–formaldehyde (PF) resin from photodegradation, thereby enhancing the effectiveness of surface coatings on PF-impregnated wood.²⁷ The combination of organic UV absorbers and HALS additives preserved the natural color of wood and provided a cooperative effect in which the organic UV absorbers converted UV energy into heat before it reached the substrate. Furthermore, HALS compounds can remove the free radicals generated by the degradation of lignin under visible light (<500 nm). The optimal combinations of HALS compounds with organic UV absorbers were found to be BTZ + HALS-1 and HPT + HALS-2,²⁸ while UVA-3 + HALS-3 protected natural wood from discoloration after 2000 h of exposure.²⁹ Therefore, the combination of organic and inorganic UV absorbents with HALS compounds can more effectively reduce the effect of light on the wood surface than any one component alone. In addition, a BTZ + HALS + TiO₂ + ZnO combined treatment provided superior surface color stability for four types of wood after UV irradiation for 320 h.³⁰

5. PERSPECTIVES AND CONCLUSIONS

The investment in research on the photodegradation mechanisms of bamboo and lignin has improved the understanding of bamboo degradation in outdoor environments. Previous studies have primarily relied upon artificial light sources to simulate sunlight and accelerate the aging of bamboo materials. However, this does not accurately correspond to actual aging effects. Therefore, establishing a long-term, effective, and systematic natural aging database is critical for the experimental study of bamboo photodegradation. Bamboo is typically processed for use in outdoor materials including bamboo scrimber, bamboo laminated

lumber, bamboo plywood, and bamboo/plastic composites that are often treated and processed to improve their weather resistance. However, these treated materials still photodegrade to some extent. The next step in developing outdoor bamboo building materials involves studying the light-induced changes in bamboo products after treatment, which has practical significance for the efficient utilization of bamboo. The synergistic effect of multiadditive coatings should be the focus of further research, as coating treatments containing additives like UV absorbers have been shown to effectively inhibit the photodegradation of the bamboo surface. Furthermore, the fastness and elongation at the break of bamboo coatings should be considered. Future research on bamboo coatings should include multicomponent functional additives that meet the requirements of low UV light transmittance, high visible light transmittance, excellent weather resistance, low cost, easy use, and low environmental impact.

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Notes

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