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Enhancement of bamboo surface photostability by application of clear coatings containing a combination of organic/inorganic UV absorbers

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ABSTRACT

Benzotriazole (BTZ), benzophenone (BP), nano-TiO_2 ($NTiO_2$), and nano-ZnO (NZnO) are potential components of UV protection coatings due to being UV light absorbers. Herein, the UV-protective effects of four acrylic coatings containing individual organic and inorganic UV light absorbers and another four coatings containing both types of absorbers were determined by employing accelerated bamboo aging tests. Although organic absorbers decomposed during aging, their degradation rate decreased in the presence of inorganic absorbers. Moreover, individual organic absorbers were better suited for color stabilization than inorganic ones, with the best bamboo surface photostability enhancement achieved by BTZ-containing coatings (BTZ, BTZ-NZnO, and BTZ-$NTiO_2$). Furthermore, strong synergistic effects were detected for BTZ-NZnO and BTZ-$NTiO_2$, whereas an antagonistic effect was observed for BP-$NTiO_2$ and BP-NZnO. Thus, combinations of organic and inorganic UV light absorbers efficiently inhibited the degradation of the former, with the performance of clear coatings determined by the type of the organic absorber.

1. Introduction

Bamboo is extensively used as an environmentally friendly construction and decoration biomaterial due to its fast growth rate, ease of processing, high strength-to-weight ratio, attractive natural color, elegant texture, and cultural value [1,2]. However, when exposed to solar radiation without protective treatment, bamboo and its products undergo surface degradation, which primarily results in photodiscoloration [2] and deterioration of clear topcoats [3]. This behavior is ascribed to the fact that bamboo, similarly to wood, comprises a blend of polymers (lignin, cellulose, and hemicellulose) with a certain degree of light absorption capacity [4,5], which leads to the occurrence of photochemical reactions. Specifically, lignin is particularly sensitive to solar radiation due to featuring an absorption peak at 280 nm, with its tail extending to 400 nm and further into the visible region [6]. On macroscopic damage, the lignin-rich middle lamellae are always rapidly eroded upon prolonged UV light exposure [7], with considerable cracking observed in the secondary walls of moso bamboo (*Phyllostachys pubescens*) after 160-h irradiation [2]. At the same time, water accelerates the loss of soluble lignin degradation products, since the loosened surface fibers are directly exposed to UV radiation [7]. Thus, rubberwood (*Hevea brasiliensis*) surface delignification was reported to occur after one-day exposure, being almost complete after one week [8]. Wang compared the photodegradation rates of bamboo (*Phyllostachys pubescens* Mazel) and two wood species, revealing that the former was less influenced by photoirradiation due to its lower lignin content, with the color changes of all materials being well correlated with lignin degradation and carbonyl compound formation [1].

Although UV (286–380 nm) light accounts for only 5% of the solar radiation, its energy is sufficient for cleaving many chemical bonds, e.g., C—C, C—O, and C—H ones [7]. As mentioned above, lignin contains moieties that interact with UV light and form chromophores, absorbing 80–95% of the UV light and thus undergoing photodiscoloration [6,9]. Hence, among all environmental factors, UV light exposure is the most significant contributor to bamboo surface degradation [10], being signified by surface discoloration [1,11–13].

Materials can be effectively protected by blocking UV light from reaching their surface using appropriate coatings. When color stabilization of natural bamboo surfaces is required for decorative end-use (floors, panels, furniture, etc.), the easiest and most common method of inhibiting the UV light-induced photodegradation of lignin is the application of UV light absorber-containing films on the exterior object

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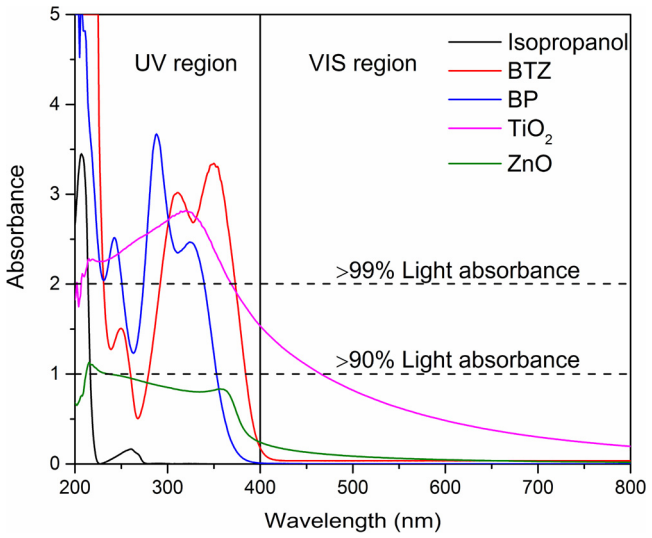

Fig. 1. Spectra of 0.01 wt% UV absorbers dispersed in isopropanol.

surface. (Meth)acrylic polymers are widely used as binders in the formulation of paints and surface coatings due to their excellent properties [14], with acrylic resin being recognized as the main film-forming agent due to its high weathering resistance, transparency, and good gloss and color retention. However, acrylic resin exhibits a low UV light blocking capacity, with its application in protective bamboo coatings requiring the addition of organic and inorganic UV light absorbers. In particular, organic UV light absorbers based on triazine (HPT), benzotriazole (BTZ), and benzophenone (BP) scaffolds are extensively used for the stabilization of polymeric materials [3,5,15–18]. Although HPT outperforms BTZ in artificial and outdoor weathering tests, the application scope of the former may in some cases be limited by its light yellow color [5]. Conversely, BTZ and BP feature two absorption peaks in the UV region, barely absorbing visible light and thus being more suitable for the preparation of transparent UV-shielding coatings (Fig. 1). The development of nanotechnology has made mineral UV screeners such as ZnO, TiO_2, and Fe_2O_3 increasingly popular components of transparent coatings due to their excellent stability toward long-term aging, high specific surface area [19], and broad absorption in both UV and visible regions (Fig. 1) [5,12].

However, coatings containing individual organic or inorganic UV light absorbers feature certain disadvantages, e.g., individual organic UV light absorbers exhibit strong absorption only in the UV region (Fig. 1), whereas lignin can also be degraded by visible light with wavelengths of up to 500 nm [20,21], with aging-induced self-degradation also resulting in the decrease of absorbance capacity [3]. The degradation rate of UV light absorber–containing clear coatings can be reduced by using hindered amine stabilizers to formulate coatings [3]. On the other hand, inorganic UV light absorbers can also absorb visible light, thus decreasing coating transparency. In addition, organic absorbers are commonly characterized by poor thermal stability, e.g., BP has a melting point of only 48–49 °C. As another example, the light scattering ability of TiO_2 exceeds that of ZnO due to the higher refractive index of the former ($n(TiO_2) = 2.6$, $n(ZnO) = 1.9$), and thus, clear coatings comprising TiO_2 have a more hazy appearance. The screening efficiency of TiO_2 and ZnO is also increased by decreasing particle size [22], with proper dispersion of nanometer-sized inorganic absorber particles in organic polymer resins to form composites coatings being a hard-to-reach prerequisite for achieving maximum efficiency [23,24]. Besides, the photocatalytic activity of TiO_2 and ZnO (leading to the formation of reactive free radicals) is unfavorable for coating-related applications [23]. The dispersion and photocatalytic activity of ZnO nanoparticles can be improved by surface-grafting of polystyrene, which, however, results in reduced UV–vis absorption capacity [25]. To circumvent the disadvantages of individual organic or inorganic UV light absorbers, coatings comprising combinations of both absorber types were prepared by a sol-gel method and were shown to exhibit significantly reduced light transmission over the whole UV region [26]. Moreover, the combination of inorganic and organic absorbers was also reported to synergistically enhance coating gloss [12]. Therefore, it was hypothesized that the performance of a combination of organic and inorganic UV absorbers might surpass those of individual constituents.

This study describes the effects of single-component (BTZ, BP, nano-TiO_2 ($NTiO_2$), and nano-ZnO (NZnO)) and two-component (BTZ-$NTiO_2$, BTZ-NZnO, BP-$NTiO_2$, and BP-NZnO) UV light absorbers on the UV light resistance of an acrylic-based bamboo exterior coating. Organic absorbers were employed as powders, and inorganic nanoparticles were pre-dispersed in isopropanol by physical blending before addition to the acrylic resin. Eight coatings containing different absorbers were deposited on quartz glass to form free films, and uncoated bamboo specimens covered with these films were subsequently exposed to UV light. Finally, the synergistic and antagonistic effects of organic/inorganic absorber combinations on the performance of clear coatings were evaluated.

2. Materials and methods

2.1. Bamboo specimens and coating formulations

Periderm and inner tissue–free bamboo strips were obtained from a four-year-old moso bamboo plant (*Phyllostachys pubescens* Mazel) harvested at a plantation located in the Zhejiang province in southern China. All knot-free bamboo blocks measuring 40 mm × 15 mm × 5 mm (length × width × height) were cut out from the same section of bamboo culm. Subsequently, specimens were sanded using a 120-grain-size sand paper and conditioned to a moisture content of ~12%.

Acrylic resin, cyclohexane, and two surfactants were used to prepare a clear-coat resin (Table 1) with a 57% solid content of acrylic resin. Further information on organic and inorganic UV light absorbers added to the clear-coat resin is provided in Table 2. To exclude the effects of other additives on photostabilization performance, only small amounts of cyclohexane and anhydrous alcohol were used in formulations as dispersants. Table 3 lists the eight employed coating formulations, denoted as A–H. A blank coating comprising the clear-coat resin and anhydrous alcohol was used as a control. Coatings A–D contained one absorber, while coatings E–H contained two absorbers at equal concentrations. Each coating was prepared in a quantity of 20 g.

2.2. Preparation of bamboo samples covered with films

To prepare free films, coatings were applied on quartz glass substrates with dimensions of 42.5 mm × 15 mm × 1.2 mm using a tetrahedral wet film preparation apparatus (SZQ, AI Testing Instrument Co., Ltd., Taizhou, China), with the thickness and area of the wet film equaling ~75 μm and 40 mm × 10 mm, respectively. After curing at room temperature, the weight of the dry film approximately equaled 0.0050 ± 0.0004 g, and a portion of the thus produced dry film was peeled off for subsequent experiments. According to Chang and Chou

Table 1
Clear-coat resin composition used in this study.

Additives	wt%	Supplier
Acrylic resin	86.21	Taiyuan Saisili Fine Chemical Co., Ltd., China
TWEEN® 40	2.30	Aladdin Industrial Corporation, China
Span 80	2.30	Sinopharm Chemical Reagent Co., Ltd., China
Cyclohexane	9.19	Hangzhou Lanbo Industrial Co., Ltd., China

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