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Evaluation of UV-permeability and photo-oxidisability of organic ultraviolet radiation-absorbing coatings

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ABSTRACT

Enhancing the durability of the coatings used on bamboo products is essential for increasing their use in outdoor environments. In this study, we investigated organic UV radiation-absorbing coatings for use on bamboo surfaces. The degree of resistance of the coatings, which contained 2-(2-hydroxy-3-tert-butyl-5-methyl-phenyl)-5-chlorinated benzotriazole (BTZ-1), to UV radiation degradation was determined through spectroscopic analysis. The critical BTZ-1 loading amount was determined by analysing the spectroscopic data. Fourier transform infrared spectroscopy was used to elucidate the relationship between the degree of photooxidation of the coatings and their BTZ-1 concentration. The experimental results showed that the coatings provided a high degree of shielding from UV radiation. The critical loading amount was determined to be 1.82 ± 0.05 g BTZ-1/m^2. The coatings formed using the formulations that contained 3 and 5 wt% BTZ-1 exhibited the lowest degree of photooxidation after exposure to UV radiation.

1. Introduction

Bamboo is well recognised as a sustainable ecological material and is used widely owing to its attractive natural colour, beautiful texture, ease of processing, and high strength-to-weight ratio. [1] However, when bamboo is exposed to outdoor conditions that result in weathering, such as solar radiation, moisture, oxygen, high temperatures, and bacteria and fungus, its exterior tends to undergo discoloration and loses its glossiness. Further, it also loses its strength and adhesiveness, becomes rougher, and exhibits chalking [2–6]. Among the above-listed factors, solar radiation, especially ultraviolet (UV) radiation, contributes the most to the degradation process. Therefore, it is essential to develop UV radiation-resistant coatings for bamboo.

The UV radiation that reaches the surface of the earth can be subdivided into the UV-B (280–320 nm) and UV-A (320–400 nm) ranges. The energies of UV-B and UV-A photons are higher than those of the photons of visible and infrared radiation, as they have a shorter wavelength. Further, their energies also exceed the carbon–carbon single bond energy. In combination with the oxygen in the air, UV radiation is able to initiate various chemical reactions on the surfaces of exposed natural and synthetic organic substrates. The most effective technique of protecting against UV radiation is to cover the exposed surfaces with coatings to which inorganic and organic UV radiation absorbers have been added [7]. Considerable work has been done on the use of inorganic absorbers, such as ZnO and TiO_2 nanoparticles, in UV radiation-resistant coatings [8]. ZnO and TiO_2 nanoparticles have both been used in coatings to protect organic materials against UV radiation and to bestow antimicrobial properties [8]. In addition to exhibiting UV radiation-shielding and antibiotic properties, ZnO particles are known to improve the thermal stability [9] and wear resistance and increase the refractive indices of transparent polymers [3]. All of these advantages require that the particles be nanosized. However, it is difficult to homogeneously disperse nanoparticles in a coating while ensuring that the coating exhibits high stability and dries readily [10,11]. Modifying the surface to be coated is one way of improving the dispersion of nanoparticles in the coating. However, this may reduce the UV radiation-shielding property of the coating [12]. A few studies have indicated that ZnO and TiO_2 nanoparticles can also absorb visible light, especially over wavelengths of 400–500 nm. Therefore, they may not be the most suited materials to form clear UV radiation-resistant coatings [13,14]. It is also known that organic compounds such as benzotriazoles (BTZs), triazines, malonates, and oxalanilides also absorb UV radiation [15–21]. There have been a few comparative studies on the photostabilities of coatings to which BTZ and micronized TiO_2 have been added. It was found that BTZ was better than TiO_2 as a

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Table 1
Clear-coat resin.

Additives	Supplier	wt%
Acrylic resin	Taiyuan Saisili Fine Chemical Co., Ltd., China	64.56
Ethyl acetate	Sinopharm Chemical Reagent Co., Ltd., China	32.19
Anhydrous alcohol	Shanghai Lingfeng Chemical Reagent Co., Ltd., China	3.25

Table 2
Coating formulations.

Coatings formulation	wt% BTZ-1	BTZ-1 (g)	Clear coating resin (g)
a	0.00%	0	24.91
b	0.99%	0.27	27.01
c	3.00%	1.02	32.97
d	5.00%	1.60	30.37

UV radiation absorber. This unexpected result could be explained on the basis of the photocatalytic activity of TiO_2 [22,23].

The objective of this study was to determine the relationship between the BTZ concentration, dry coating thickness, and UV absorption of clear topcoats containing BTZ and to investigate the chemical changes induced in such coatings after weathering. A benzotriazole, acrylic resin, ethyl acetate, and anhydrous alcohol were used to form coatings with different concentrations of 2-(2-hydroxy-3-tert-butyl-5-methyl-phenyl)-5-chlorinated benzotriazole (BTZ-1). The UV radiation permeabilities of the coatings were evaluated through spectroscopic analysis. The extents of photooxidation of the coatings after weathering were determined using Fourier transform infrared spectroscopy (FTIR).

2. Materials and methods

2.1. Formulations for producing UV radiation-absorbing coatings

Acrylic resin, ethyl acetate, and anhydrous alcohol were used to prepare the clear-coat resin (Table 1). Acrylic resin, which was used as a binder, was bought from Taiyuan Saisili Fine Chemical Co., Ltd. The coating formulations used are listed in Table 2. BTZ-1 was also obtained commercially. The acrylic resin and the other additives were initially mixed with a stirrer (RW 20, IKA) at 1000 rpm for 30 min. Then, BTZ-1 was added into the clear-coat resin in the amounts listed in Table 2. The coatings were prepared at high speed (2000 rpm) using a stirrer. The 0 wt% BTZ-1 sample, which consisted of the pure clear-coat resin, was considered a control. The BZT-1 concentrations were determined on the basis of the amounts (wt%) of the BTZ-1 solids in the clear-coat resin and BTZ-1.

2.2. Preparation of the coatings

Quartz glass was cut into slides with dimensions of 45 mm × 12.5 mm × 1.2 mm. These plates were used as substrates for the clear coatings. Clear coatings of the homogenous formulations were coated on the quartz glass slides; the amounts of the formulations used were 0.022 g, 0.046 g, and 0.073 g. Prior to the application of the coatings, the formulations were stirred for 8 min using a magnetic stirrer (78HW-1). Next, the slides were covered with clear coatings of the formulations at a temperature of 20 °C and allowed to rest until most of the air bubbles had been eliminated; this took approximately 10–20 min. The resulting films, which were 12 in number, were dried in air at a temperature of 20 °C for 24 h. They were then heated at 135 °C for 2 h to accelerate curing of acrylic resin prior to being analysed.

2.3. Viscosities of the coating formulations

The viscosities of the coating formulations were measured with a viscometer (NDJ-8S) at a temperature of 27 °C. The number of rotor was 27.

2.4. Thicknesses and weights of the dried coatings

The thicknesses of the glass slides were measured before and after the coating process (b_{slide} and $b_{slide+film}$, respectively) using a Vernier calliper (accuracy of ±0.01 mm). The thicknesses of the dry coatings (b_{film}) were calculated using Eq. (1).

$$b_{film} = b_{slide+film} - b_{slide} \quad (1)$$

The glass slides were weighed before and after they had been coated (m_{slide} and $m_{slide+film}$, respectively). The weights of the dry coatings (m_{film}) were calculated using Eq. (2).

$$m_{film} = m_{slide+film} - m_{slide} \quad (2)$$

2.5. Spectroscopic analysis of the coatings

The UV spectra of the coatings were obtained using a UV-Vis spectrophotometer (UV-2401 PC). The glass slides were sized to exactly fit the sample cell of the spectrophotometer, and the samples were scanned for wavelengths of 200–700 nm in increments of 1 nm and middle speed.

2.6. Weathering and FTIR analysis of the coatings

The coated slides were placed outdoors in Hangzhou city (120.2 E, 30.3 N) to be weathered. The number of clear days in Hangzhou during March 3 to September 3, 2014 when samples were weathered was 23. The mean maximum air temperature and minimum air temperature of Hangzhou during weathering period was 26.5 °C, 18.7 °C, respectively (climate data collected by a small weather instrument CG-01). After being aged for 6 months, the coatings were scraped off and ground. Then, their FTIR spectra were recorded using an FTIR spectrophotometer (Nicolet iS10) in the absorbance mode over frequencies of 4000–400 cm^{-1}, a KBr pellet was employed during the process. The powdered coatings were mixed with KBr in a weight ratio of approximately 1:50. Pellets of this mixture were formed at the same pressure and same treatment time.

3. Results and discussion

3.1. Viscosity, dry-coating thickness, and coating weight

The viscosities of the coating formulations containing different concentrations of BTZ-1 are presented in Fig. 1. The viscosity of the control, which did not contain BTZ-1, was 320 mPa S. In comparison, the viscosity of the 5 wt% BTZ-1 sample was 414 mPa S. This was 96 mPa S higher than that of the control. This suggests that the BTZ-1 concentration had an effect on the viscosity of the coating formulations. It is also found that there was a linear relationship between the BTZ-1 concentration and the viscosity. The shrinkage ratio (i.e., the ratio of the BTZ-1 concentration to the viscosity) for the samples was determined to be 18.867%. This also illustrates that there existed a positive correlation between viscosity and concentration. The thicknesses of the coatings were measured at three locations using a Vernier calliper. The measured values were averaged and compared with those of the other samples (Fig. 2). A linear relationship was observed between the amounts of the formulations used for the coatings and their thicknesses. Further, the