



Enhanced the weatherability of bamboo fiber-based outdoor building decoration materials by rutile nano-TiO₂



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HIGHLIGHTS

- The photostability and thermal stability of bamboo fiber/HDPE composites were definitely enhanced by rutile TiO₂.
- Both the positive and negative effects of nano-TiO₂ on the weatherability of the composites were analyzed.
- Nano-TiO₂ showed clearly impacts on the properties and structures of the composites.

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ABSTRACT

This paper analyzes the impact of rutile nano-titanium dioxide (nano-TiO₂) on the weatherability of bamboo fiber/high-density polyethylene (HDPE) composites using xenon-arc weathering accelerated tests. The results showed that a series of performance reduction containing color fading, surface cracking, structural transformations and loss of mechanical properties appeared on the composites during the accelerated weathering process. These attributes could be minimized to a greater extent using rutile nano-TiO₂. The analysis revealed that, although free-radicals created by nano-TiO₂ after absorbed UV light may resulted in the oxidization of bamboo fiber and HDPE, rutile nano-TiO₂ mainly acted as light screening agent and ultraviolet absorbent, which retarded the photo-oxidative of the composites. Moreover, rutile nano-TiO₂ enhanced the thermal stability by interacting with the molecular chain of bamboo fiber and HDPE which resulted into reduced thermo-oxidative aging of composites.

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1. Introduction

The 1990s witnessed a burgeoning interest in the development of industrial and consumer products that combine lignocellulosic fibers and plastic [1]. In the past two decades, more and more wood-plastic composites (WPC) were employed as exterior building materials such as decking, siding, railing, fences, window and door frames which had combined the advantages of wood and plastic having characteristics such as long-term performance, cost-effectiveness, shape flexibility and “carbon footprint” [23,19], were employed as exterior building materials, such as decking, siding, railing, fences, window and door frames, etc. The global WPC

market has experienced double-digit growth in North America and Europe, and the demand for WPCs in the United States has reached to \$2.4 billion in 2013 [38,14]. Such attention is not only because of environmental concerns, but also of the necessity of providing a high-performance, multi-functional product at a low-cost. Bamboo is an abundant natural resource in Asia and South America, and is gaining worldwide renown as a potential reinforcement for polymer composites because of its innate properties such as low density, high tensile modulus, and low elongation at break [39]. The superior mechanical properties of bamboo are mainly attributed to its unidirectionally oriented fibers, which account for 40% of the culm by volume [40]. Moreover, bamboo only takes several months to grow [24], whereas wood needs more than ten years. The reported growth rate of bamboo may seem unbelievable, but the fastest-growing bamboo can vertically grow at a rate of two inches per hour. In particular moso bamboo species, a height of 60 feet can be achieved in just three months [2].

Despite the increasing demand for WPC by consumers, growth in its exterior applications has raised a concern about their

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resistance to weathering. Since both wood fiber and polymer matrix experience photo-degradation upon exposure to sunlight, especially during ultraviolet light, weathering of WPCs results in severe discoloration and a modest loss in mechanical properties [6,7,4,33,5,3]. The aesthetic value, as well as the useful value, of WPCs is compromised through weathering, making it a major concern. Therefore, when a new WPC material is developed, it is important to evaluate changes in its properties under a variety of environmental conditions such as UV light and moisture [21], to assess effects influencing useful service life [8,26].

Based on the mechanisms of the aging of WPCs, it can be concluded that the key to control the aging of WPCs is shielding the effects of UV lights. Many studies have focused on light stabilizers such as benzophenone, benzotriazole, amines, phenolics, and phosphites antioxidants [31,22,35], which can restrain or eliminate the photochemical reaction of WPCs during the weathering. These organic light stabilizers definitely improve the weatherability of WPCs, but many drawbacks are raised in services such as compatibility, migration, or decomposition during UV exposure. Moreover, international regulatory authorities concern about the migration of light stabilizers additive from consumer products such as food, drug, hygiene, and cosmetic packaging, the possible release of organic light stabilizers by the WPCs should be controlled and minimized [37,15]. In order to overcome the above mentioned drawbacks, the inorganic light stabilizers, such as titanium dioxide (TiO_2) and zinc oxide (ZnO) have attracted great attention in the recent years. Compared to the instability of organic anti-oxidants, the inorganic UV absorbers exhibit a non-toxic and chemical stability under exposure to both UV irradiation and high temperatures [28,13].

Many studies have shown that TiO_2 nanoparticles provided effective UV absorption ability and also regarded as safe material for human beings and animals [30,29,11]. But nano- TiO_2 , with high photocatalytic activity, might create free-radicals after absorbed UV light, may result in the oxidization of WPCs and quality degradation. Therefore, in this study, the bamboo fiber/HDPE composites/rutile nano- TiO_2 composites were prepared and the effects of rutile nano- TiO_2 on the weathering resistance of the composites and its mechanism were evaluated and analyzed from multiple perspectives.

2. Experiment

2.1. Materials

Moso bamboo fiber (the length varied from 100 to 150 μm and provided by Research Institute of Comprehensive Utilization of Biomaterials, Huazhong Agricultural University, China) was first dried at 105 °C for 48 h. HDPE (5000 s), a product of Daqing Petrochemical Co. with a melt index of 0.7 g/10 min and density of 0.950 g/cm³, was used without any treatment. Rutile and anatase nano- TiO_2 (40 nm), obtained from Aladdin reagent Co., Ltd., Wuhan, China, was dried in vacuum at 105 °C for 48 h before use. Absolute ethyl alcohol, titanate coupling agent (NDZ-201) and poly (ethylene-co-vinyl acetate) (EVA) were analytical grade and used as received.

2.2. Samples preparation

Nano- TiO_2 (6 g) were added to a beaker with 450 mL absolute ethyl alcohol, and dispersed at 600 W for 30 min by using an Ultrasonic Processor FDL-1200 (intermittent dispersion of pulsing on for 1 s and off for 2 s, with a frequency of 20 kHz). Bamboo fiber (40 g), HDPE (60 g) and EVA (10 g) were then added to solution, which was then stirred using a motor stirrer at high-speed (>1000 rpm) at 90 °C until the alcohol evaporated completely. The mixture

was then poured into a kneading machine and thoroughly kneaded for 1 h. Finally, the composite was hot compressed into 1.2 and 4.0 mm thick sheets at 170 °C under 20 MPa, and was coded as BHTi when the composite without nano- TiO_2 was coded as BH.

2.3. Accelerated weathering test

Accelerated weathering tests were conducted by using xenon-arc weatherometer. Bamboo fiber/HDPE specimens (100 mm × 100 mm × 1.2 mm) were subjected to an accelerated weathering procedure as outlined in Chinese standard method GB/T 16259–2008 included a 120 min cycle consisting of 102 min xenon-arc radiation at 65 °C (average irradiance was 0.35 W/m²) and 18 min water spray.

2.4. Colorimetric analysis

Color measurements of weathered bamboo fiber/HDPE specimen surfaces were recorded using a Minolta CR-400 Chroma Meter (Minolta Corp., Japan). The CIELAB color system was used to measure the surface color in L*, a*, b* coordinates.

2.5. Surface morphology analysis

Field emission scanning electron microscopy (FESEM) was performed with a JSM-630 LV scanning microscope operating at 30 kV. Prior to the analysis, the surfaces were covered with a layer of gold using a sputter coater.

2.6. Mechanical properties

The bending strength and bending modulus of the composites were determined by using a Tianyuan NTY8000 electron tensile tester (Jiangsu Tianyuan Test Equipment Co., Ltd., China) according to the Chinese standard method GB/T 9341–2008 (Plastic-Determination of flexural properties).

2.7. Photocatalytic activity analysis

Nano- TiO_2 (0.3 g) were added in methylene blue solution (1.0×10^{-5} mol/L) and then exposure to xenon-arc irradiation (average irradiance was 0.35 W/m²). The photocatalytic activity of nano- TiO_2 was evaluated by the degradation rate of methylene blue, which monitored by using a Shimadzu UV-1700 spectrophotometer (Shimadzu, Kyoto, Japan).

2.8. Fourier transform infrared spectroscopy analysis

Changes in the carboxylic acids, ester and vinyl concentrations during weathering were monitored by a Nicolet (USA) Nexus 470 Fourier transform infrared spectroscopy (FTIR). The powdered samples were blended with potassium bromide (1:100) and laminated. The wave range, from 4000 to 400 cm⁻¹, was scanned 32 times for spectrum integration, and the scanning resolution was 4 cm⁻¹. The concentration of carboxylic acids, ester and vinyl groups present in the weathered bamboo fiber/HDPE composites was determined using the Beer–Lambert equation with some assumptions [18], as Eq. (1).

$$A = \varepsilon bc \quad (1)$$

where A is the absorbance of the functional group band in the FTIR, c is the molar concentration of the functional group, ε is the molar absorptivity, and b is the path length through the sample. Lacoste et al. [18] reported that the ε of model carboxylic acids (1718 cm⁻¹), esters (1744 cm⁻¹), and vinyl (1635 cm⁻¹) were 350, 590 and 121 L/mol/cm, respectively.

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