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The interface designing and reinforced features of wood fiber/polypropylene composites: Wood fiber adopting nano-zinc-oxide-coating via ion assembly

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Wood-plastic composites (WPCs) with excellent water resistance, light absorption, mechanical properties, and thermal stability features were fabricated on an assembled nano-interface using cationic polyethyleneimine-nano-ZnO (PEI-ZnO) and anionic sodium polyacrylate-wood (PAAS-wood). The charge grafting, assembly, and dispersive morphology on the wood surface were analyzed by ZETA potentials, SEM images, crystal features, XPS and FTIR spectra. With a three dimensional shielding-assembling nano-network, water absorption of wood-polypropylene composite decreased from 5.20 wt.% to 1.83 wt.%, and the decomposition temperature (Td) of wood and polypropylene were enhanced by 114 °C and 63 °C depending on passing and hindering. The tensile strength and the glass transition temperature (Tg) were enhanced from 20.42 MPa, 11.7 °C to 38.73 MPa, 33.21 °C, respectively, likely due to firmed nano-dispersion, strong interfacial adhesion, and sufficient load transfer. In addition, ultraviolet and near-infrared resistance of the composite were found to be promoted by adopting the assembled nano-interface.

1. Introduction

Interest in Wood-Plastic-Composites (WPCs) reinforced with structure treatments has increased due to their potential practical properties, including mechanical properties, ultraviolet resistance, and hydrophobicity, facilitating the use of these materials in nano-modification, micro-encapsulation and interfacial couplings [1–8]. Nanoscale inorganic fillers with an average particle size smaller by at least an order of magnitude compared to conventional fillers used in WPCs are becoming commercially available. However, significant challenges remain for the development and application of high performance nano/WPCs including (i) the need for uniform dispersion of nano-particles in WPCs matrix and (ii) strong interfacial interactions to effectively load transfer from the WPCs matrix to nano-structure [8]. Compared with physical addition, due to economical and practical aspects, surface nano-growth is used preferentially in wood products to achieve more stable nano-dispersion. There is interest in the development of in-situ deposition for stable coatings consisting of nano-particles on wood surface, driven by their excellent characteristics of mechanical and thermal performances, optical behaviors, and bactericidal resistance. For instance, Caichao Wan reported Graphene nanosheets were successfully in situ deposited on the surface of a wood matrix via a mild fast one-pot hydrothermal method [9]. The wood was evenly coated by a dense uninterrupted multilayer graphene nanosheets structure, which was efficient in both UV-resistance and thermal stability. A similar cosolent-controlled hydrothermal method was also adopted by Qingfeng Sun who reported a firm nano-TiO_2 coating that served as a protective layer to prolong combustion [10]. In addition, based on the reports by C.Q. Peng and M. Agarwal, self-assembly via ion absorption was used on a pulp surface to construct a efficient conducting network [11,12]. Mechanical and in-situ nano-dispersion have a strong tendency to agglomerate and can not be controlled sufficiently. Thus, nano-assembling of a stable nano-interface may be a better strategy for WPC production.

Nano-Zinc Oxide (ZnO) is low cost, non-toxic, has high chemical stability, and the ability to absorb or scatter UV irradiation. This

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material has potential use as a filler for composite, as demonstrated by some previous reports [13–16]. The cell wall of wood is mainly composed of biopolymers, including cellulose, lignin and hemicellulose, and there are a large number of hydroxyl groups on cellulose. Chemical assembly can advantage of this structure making use of the hydroxyl groups on the surface of wood fiber with active nano-ZnO, to construct an efficient nano-coating on the wood surface, allowing construction of a dispersive three-dimensional nano-interface in WPCs. In terms of ionic self-assembly, this work used cationic polyethyleneimine-ZnO (PEI-ZnO) and anionic sodium polyacrylate-wood fiber (PAAS-wood). The reasons for these selections are as follows: branched PEI with high electric density and activity can allow reaction of inorganic particles with the hydroxyl groups on surface, efficiently making nano-ZnO cationic. Most importantly, in the process of ion assembly, the grafted PEI-coating structure enhances macroscopic smelting between wood fiber and polypropylene for its viscosity and liquidity [17,18]. PAAS has excellent adhesive properties, and is endowed with excellent flocculent ability for its active anions ($-COO^-$) [19]. By grafting on wood surface, followed by ultrasonic treatment, cationic PEI-ZnO particles would be absorbed by PAAS-wood.

In the present work, the assembling process adopted ultrasonic technology. By testing different assembling ratios, ion assembly was evaluated by ZETA potentials, nano-size, crystal features and absorptive structure. Additionally, particle emphasis was also placed on examining the internal mechanism of the dispersive nano-network in WPCs as well as the relative functions of wood-polypropylene composite, including dimensional stability, light absorption, mechanical reinforcements, and thermal shielding.

2. Materials and methods

2.1. Materials

Polypropylene (PP) particles were obtained from Dushanzi petrochemical company of china petroleum (Q/XJ 1100-1998 T30S, diameter: 3 mm). Poplar fiber was obtained from Shanghai Jia Feng, Ltd (diameter: 5–20 um). Sodium polyacrylate (PAAS) with 40 wt.% solid content was obtained from Sinopharm Chemical Reagent Co., Ltd (SCRC). Branched ethylene imine polymer (PEI, relative molecular mass of about 7000) and nano Zinc Oxide (ZnO, diameter: 50 ± 10 nm) were purchased from Aladdin Industrial Corporation (China).

2.2. Synthesis

Wood fibers and polypropylene particles were dried at 110 °C for 10 h to eliminate moisture. Next, wood fibers were dispersed in PAAS solution (pH value = 10, 16 g wood fibers in 500 ml of 0.2 wt.%, 0.4 wt.%, 0.6 wt.%, 0.8 wt.%, or 1.0 wt.% PAAS solution) and nano-ZnO particles were dispersed in PEI solution (0.4 g, 0.8 g, 1.2 g, 1.6 g, or 1.8 g in 250 ml-8 wt.%-PEI solution), the ultrasonic time (50 °C) was 1, 3, or 5 h, respectively. The resulting wood fibers and nano-ZnO particles were washed and isolated by filtration five times, and assembled with each other for 3 h at 50 °C. The assembly adopted wood fibers grafted in 0.4 wt.% PAAS solution (3 h) and exhibited different ratios of cationic nano-ZnO. After washing and isolation, the assembled wood (16 g) was melted with dried polypropylene (24 g) at 175 °C in a torque rheometer. For avoiding wood decomposition, the success of smelting occurred when the shearing interaction and the torque-curve value became stable. The final mixture was formed into a sheet shape using a plate rheometer at 180 °C under pressure of 5 MPa, 10 MPa, or 15 MPa per 3 min.

2.3. Functional characterization

The morphology was observed under a sirion-200 scanning electron microscope (SEM, FEI, America) with an accelerating voltage of 10 kV. Structure analysis based on chemical assembly was examined by a Nicolet Nexus Fourier transform infrared spectrometer (FTIR). Crystallization features were studied by X ray diffraction (XRD). For the wood-polypropylene composite, the weight ratio of the nano-ZnO mentionaed above was 1 wt.%, 2 wt.%, 3 wt.%, 4 wt.%, or 5 wt.%. At room temperature (25 °C, 101.3 kPa atmospheric condition), the contact angle was tested by a contact angle meter SL200A (Solon shanghai Co., Ltd.) with 2 uL water droplet, and after drying at 110 °C, the water absorption was evaluated five according to formula (1) °C for 24 h:

$$A\% = \frac{W_s - W_p}{W_p} * 100\% \tag{1}$$

where W_s, W_p are the weight of the primary composite and swelling composite respectively. Tensile properties (GB/T 1040-92: 50 mm * 20(10) mm * 3 mm) and flexural properties (GB 1042-79: 50 mm * 15 mm * 3 mm) were determined by a CMT 4204 universal material testing system (Shenzhen SANS Test Machine Co., Ltd, China) at room temperature with crosshead speed of 20 mm/min. The values reported here represent an average of the results of ten tests. Viscoelasticity was measured by the dynamic mechanical tester (DMA, tensile size: 20 mm * 6 mm * 1 mm) with −50 °C–160 °C range, the protecting gas was N_2 and heating rate was 1 °C/min at 5 Hz. The thermal decomposition of composites was analyzed by the TG with 50 °C–800 °C range using N_2 as the protecting gas. The light separation was measured by an ultraviolet-infrared spectrophotometer using 1 mm plate sample. Relative analysis referred to the Formula (2) and Formula (3):

$$T = \frac{I}{I_O} = \exp\left(-\left[\frac{3V_p x r^3}{4\lambda^4}\left(\frac{n_p}{n_m} - 1\right)\right]\right) \tag{2}$$

where T is transmittance of nano-composite, V_p is nano-volume, x was optical path, λ is wavelength of incident light, n_p and n_m are refractive index of matrix and nano-particles, r is diameter of nano-particles.

$$\delta = \frac{4E_1}{3N} \propto \left(d^2\right)^{-1} \tag{3}$$

Kubo theory: δ is gap; E_1 is Feimi energy, N is total number of conductive electron; d is supermicro-particle size.

3. Results and discussion

3.1. Nano-ZnO-coating based on ion absorption (chemical-assembly)

The experimental design is shown in Fig. 1. The grafting effect allows anionic PAAS-wood to assemble the cationic PEI-ZnO particles, resulting in a firmed and dispersed nano-surface [20,21]. With high crystallinity, long polymer chain structure, and high mass fraction (~50%), the wood strength is mainly dependent on cellulose, which was observed mainly in an I crystal form ((001) and (112)). Nano-ZnO is a six-party zinc crystal system, in which four Oxygen atoms surround a Zinc atom. The n-semiconductor and relative X-ray diffraction peaks focused on (100), (002), (101), (102), (110), (103), (112). Grafted by polyelectrolyte, in Fig. 2, it is worth noting that the crystal structure of wood and nano-ZnO did not change obviously, suggesting that the relative performance of