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PLA toughened by bamboo cellulose nanowhiskers: Role of silane compatibilization on the PLA bionanocomposite properties

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ABSTRACT

To toughen brittle poly(lactic acid) (PLA) composites, surface-modified bamboo cellulose nanowhiskers (BCNW) were introduced into a PLA matrix. The BCNW was treated with (3-mercaptopropyl)trimethoxysilane (A-189) at five concentrations between 1 wt% to 16 wt% to improve compatibility. Silylated BCNW-toughened PLA composite films were further fabricated by solution casting. The coupled reaction between A-189 and cellulose *via* Si-O-C bonding and hydrogen bonding was confirmed. BCNW was silylated uniformly and maintained its original morphology. With increasing concentration, BCNW became smooth; however, with excessive coupling agent, the BCNW surface became rough. Elongation at break was inversely proportional to tensile strength and tensile modulus. Elongation at break increased to 250.8% after the 4 wt% A-189 treatment compared to 12.35% with untreated composites. The C/O ratio of BCNW decreased after coupling agent treatment. There were physical interlocks and hydrogen bonding between two phases. A wire-drawing phenomenon was observed on the tensile fractural surface. The thermal degradation stability decreased with the increasing treatment concentration.

1. Introduction

Poly(lactic acid) (PLA) is a green polymer synthesized from lactic acid, a compound that can be derived from renewable plant resources such as corn and potato starch [1]. In recent decades, much attention has been paid to environmentally friendly nanocomposites as alternatives to petroleum-based materials due to the depletion of petroleum sources and environmental issues [2,3]. PLA is such an alternative because it is thermoplastic and can be processed by extrusion, injection molding, blow molding and thermoforming using common processing equipment similar to polypropylene, polyethylene and other synthetic polymers [1]. Its products include films, sheets, bottles and various thermoforms. Among biodegradable polymers, PLA is the most rigid and has low toughness [4]; the tensile elongation at break is usually below 20% [5]. Therefore, to expand the application of PLA (e.g., to agricultural films, garbage bags, plastic bags, food containers, food packaging etc.) toughening modification is imperative. Introduction of natural cellulose nanoparticles as reinforcing fillers in a PLA matrix has attracted increasing attention [2,3,6–9]. The advantage of using natural nano-materials modification is that small amounts of filler improve the toughness of PLA and maintain the fully degradable properties of the composite. Hossain et al. [7] attached cellulose nanowhiskers to the surface of wire-drawn PLA and found that the mechanical properties and cell biocompatibility greatly improved; Fortunati et al. [10] extracted cellulose nanowhiskers from *Posidonia Oceanica*, surface-modified with silane, and found that the elongation at break improved 100.9%. Qu et al. [11] employed 3-methacryloxypropyltrimethoxysilane to modify pulp cellulose nanowhiskers and compounded with PLA. Mechanical results showed that the tensile strength was improved, but the elongation at break was still low. Thus, the improved tensile properties of PLA with nanocellulose needs further improvement, necessitating the design of new surface chemistry and a better understanding of its effects on interfacial bonding mechanisms.

Moso bamboo (*Phyllostachys heterocycla*) is a common forest resource that grows abundantly in many tropical and subtropical regions in the world, especially in Zhejiang Province, China [5]. Bamboo residue is a good source of renewable nano-filler namely bamboo cellulose nanowhiskers (BCNW). Although cellulose nanowhiskers have shown great performance as mechanical

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reinforcing fillers, the large amount of hydrophilic hydroxyl groups on the surface of BCNW leads to poor compatibility with hydrophobic polymer matrices (e.g., poor dispersion and weak interfacial adhesion with polymer), which is great obstacle to reaching their theoretical potential [12]. BCNW can be chemically modified by a coupling agent so that hydrophobic functional groups are grafted onto the surface, which will improve the interfacial compatibility with the PLA matrix. There are two types of silane surface-treating approaches. One is cellulose is treated with different concentrations of silane alcohol aqueous solution. Qu et al. [11] employed 0.5–2.0 v/v% silane coupling agent (A-174) into ethanol, and found that 1.0 v/v% of solution-modified nanocellulose had the best effect; Saini et al. [13] hydrolyzed (3-aminopropyl) trimethoxysilane (A-1100) with different concentrations of alcohol aqueous and acetone solutions, and the suitable concentration was 50 g/L. Rojo et al. [14] also investigated different concentrations of A-1100 (1–4 v/v%) and 3-(2-aminoethylamino) propyltrimethoxysilane (AA-1100) (0.5–3 v/v%) treating eucalyptus fibers and showed that 2.2 v/v% A-1100 and 1.5 v/v% AA-1100 had good effect. Second, the usage amount of silane coupling agent can be determined according to the mass ratio of fibers. Chruściel et al. [15] reviewed silane coupling agent modification in the polymer field and found that the second approach improved the efficiency of treatment. Sun et al. [16] grafted 2.0 g of halloysite nanotubes with 0.1 g, 0.4 g, 2 g and 10 g of A-1100 and found the proper amount was below 0.4 g. The concentration of coupling agent is closely related to the number and density of surface functional groups on cellulose [17]. Thus, a proper amount helps to improve both the interfacial property and the economic effectiveness. Additionally, surface modification will decrease the intrinsic strength of cellulose, and the grafting degree of the functional groups will be affected by the coupling agent contents. Excessive content leads to self-polycondensation of the coupling agent, whereas the silylation reaction is insufficient with over lowering content [18]. As a result, it is critical to select the appropriate treating content and adjust the degree of chemical modification on the surface of BCNW, to keep original strength as much as possible and to reduce the hydrophilicity of hydroxyl group to the greatest extent. The (3-mercaptopropyl)trimethoxysilane (A-189) is a commonly used silane coupling agent [19], however, the investigations on A-189 compatibilization of cellulose nanowiskers and PLA is rarely reported. The dispersion of treated BCNW, the compatibility of interfacial adhesion between BCNW and PLA, and a better understanding of its effects on toughening mechanisms need to be further studied.

Our previous work extracted and characterized BCNW from bamboo residues using acid hydrolysis [12]. In this paper, BCNW were treated with different amounts of silane A-189 and solution cast with PLA to fabricate PLA/BCNW composites. The surface characteristics of the silylated surface were studied by Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and energy dispersive electron spectroscopy (EDS) analysis; in addition, the effect of silane coupling agent contents on BCNW compatibilization was investigated. The mechanical properties, thermal properties and thermal degradation properties of the PLA/BCNW composites were characterized. The toughening mechanism of the composites was studied, and using these results, the optimal usage amount was obtained. This research results will provide basic reference data for extending the applications of PLA in engineering fields.

2. Materials and methods

2.1. Materials

Moso bamboo residues were supplied by a local bamboo processing factory, Lin'an, Zhejiang Province, China. The particles were screened through a mesh size of 100 and dried at 105 °C to constant quality for further use. PLA (4032D) was produced by the NatureWorks Corporation (USA). The density was 1.25 g/cm^3, and the relative solution viscosity was 4.00 ± 0.10. The (3-mercaptopropyl)trimethoxysilane of ACS grade was used as purchased (Aladdin, Shanghai, China). All other reagents and solvents were used as received from the commercial source without further purification.

2.2. Preparation of bamboo cellulose nanowhiskers

The extraction procedure for bamboo cellulose nanowhiskers (BCNW) followed our previous work [12]. Briefly, bamboo particles were soaked in a 4% (w/v) NaOH solution at 80 °C for 24 h, rinsed with distilled water and dried at 105 °C. Alkaline-treated cellulose was bleached with a 15% (w/v) $NaClO_2$ solution with approximately 20 drops of acetic acid at 45 °C overnight, rinsed with distilled water and dried at 105 °C. The bleaching process was repeated to give bleached white cellulose. The bleached cellulose was hydrolyzed with 65 wt% sulfuric acid for 3 h and cooled with ice to stop the hydrolysis reaction. The excess sulfuric acid was removed by centrifugation (12,000 rpm, 5 min) using a PK 120 centrifuge (ALC, Winchester, UK). The supernatant was discarded, and the precipitate was again washed with deionized water and centrifuged. This process was repeated 3 times. The material was dialyzed with tap water for 3 days to remove other ionic materials (regenerated cellulose membrane, Fisher, Shanghai, China, cut off 8000–12000 Da). BCNWs were freeze-dried (5810R, Eppendorf, Hamburg, Germany) for further use.

2.3. Bamboo cellulose nanowhiskers modification

The BCNW was treated with different contents of A-189 (A-189/BCNW: 1 w/w%, 2 w/w%, 4 w/w%, 8 w/w%, and 16 w/w%) in a water-methanol solution (alcohol/water: 80/20). The BCNW to water-methanol solution ratio was controlled at 1: 20 w/v. Before modification, the pH of the water-methanol solution was stabilized to 4 by dribbling acetic acid with constant stirring. Once pH was stabilized at approximately 4, BCNW was added. The mixture was stirred at 50 °C for 30 min, and the slurry was vacuum-filtered and washed two times with methanol and once time with distilled water. The modified BCNW were oven-dried at 60 °C for 24 h.

2.4. Fabrication of PLA/BCNW composites film

Approximately 5.0 g PLA was added to 60 mL chloroform and stirred in a 50 °C water bath until PLA dissolved completely. The solution was blended with 2.5 w/w% dried BCNW, and ultrasonic stirring to disperse for 30 min. The blended solution was cast in a self-made PTFE mold (diameter = 80 mm) and dried at room temperature for 48 h. Eventually, PLA/BCNW biocomposite films were obtained with a thickness of 0.3–0.5 mm.

2.5. Scanning electron microscopy with energy dispersive electron spectroscopy (SEM-EDS) analysis

The surface morphology of raw bamboo particles, BCNW and treated BCNW were observed using a field launch scanning electron microscopy (Nova NanoSEM 450, FEI, USA). Composites with different treatment concentrations of A-189 were observed using a field launch scanning electron microscopy (S-8010, Hitachi, Japan). All samples were coated with gold before observation. The launching voltage of the electron microscopy was 4.0 kV. The spatial elemental distribution was evaluated by SEM using non-