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Properties of Biocomposite Fibers from Cellulose Nanowhiskers and Cellulose Matrix

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Abstract

A series of self-reinforced, biocomposite fibers were successfully fabricated using Cellulose Nanowhiskers (CNWs) and cellulose matrix isolated from mulberry branch bark by wet spinning. The obtained CNWs have a diameter of about 20 nm and a length of 300-400 nm. The hybrid solutions containing less than 9 wt% CNWs were miscible according to the rheological curves. Specially, the synergistic interactions between fillers and matrix play a key role in reinforcing the composite fibers. The tensile strength and Young's modulus of composite fibers at 65% relative humidity increased from 172 to 571 MPa and 2.06 to 4.15 GPa with increasing CNWs content from 0 to 9 wt%.

Keywords: Cellulose; Cellulose Nanowhiskers; Self-reinforced; Biocomposite Fibers; Interfacial Interaction

1 Introduction

Polymer fibers are widely used in various areas where mechanical properties are an important factor. In the context of increased concern over energy crisis, there is strong wish to replace petroleum-based polymers using natural polymers from agricultural and biological renewable resource, since they are abundant, eco-friendly and biodegradable. Cellulose is one of the oldest, most abundant natural polymer on the earth. It can be converted into all kinds of regenerated materials (fibers, membranes, food casings, sponges, etc) and cellulose derivatives (ethers, esters), which have been applied as textiles, papers, foods, cosmetics, biomaterials, and so on [1, 2]. Nevertheless, the mechanical properties of cellulose-based functional materials are highly sensitive to moisture content, which limits its application.

Mulberry trees are extensively cultivated (e.g., China, India, Brazil) for their leaves as food for silkworms. Also, mulberry leaves and branches have long been used in Chinese medicine to treat fever, improve eyesight, strengthen joints, inhibit peroxidation, facilitate the discharge of urine and lower the blood pressure [3-5]. The mulberry branches must be pruned in early summer and

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winter annually. Despite its usefulness, there is no mass utilization of mulberry branch. Thousands of tons of mulberry branch are harvested for firewood or agro-waste every year, which results in resource waste and environmental pollution. Mulberry branch bark, as a major by-product of the sericultural industry, also belongs to bast fiber, and is rich in cellulose. Cellulose fibrils are the major reinforcing constituent of the plant fiber cell walls. Acid hydrolysis of native cellulose can result in the disruption of microfibrils and formation of Cellulose Nanowhiskers, (CNWs) with an average diameter in the range of 5-50 nm, hundreds of nanometers to several micrometers in length, depending on the plant source and disintegration procedure [6-8]. Recently, CNWs have been introduced into a wide variety of materials to improve their strength and modulus due to inherent properties of CNW such as renewability, environmentally friendly, low-cost, high stiffness and strength [9-17]. In some cases, the hydrophilic CNWs possessed little or no reinforcing effect when added to hydrophilic matrix. However, CNWs have improved the mechanical properties of hydrophobic polymers. Interestingly, the reinforcing ability for hydrophobic polymers was reduced when the CNWs were surface modified to obtain hydrophobic properties [16, 17]. Those results revealed that the procedure, filler-filler interactions and filler-matrix interactions significantly impacted the reinforcing capability of CNWs, and all were important factors to take into account.

In this paper, we incorporate cellulose nanowhiskers into cellulose matrix from mulberry branch bark to improve the mechanical properties of regenerated pure cellulose fiber. The self-reinforced, green biocomposite fibers were firstly fabricated by wet spinning at variable CNWs contents. The effects of CNWs on the morphology, structure, thermal decomposition and mechanical properties of the resulting composite fibers were investigated by Field Emission Scanning Electron Microscopy (FESEM), X-ray Diffractometer (XRD), Thermogravimetric Analyzer (TGA) and tensile tests.

2 Experimental Section

2.1 Materials

Mulberry branch barks (*Morus alba L.*) were obtained from Huzhou Academy of Agricultural Sciences (Huzhou, China). The chemical reagents used here were analytically graded without further purification and is purchased from Hangzhou Mike Chemical Agents Co. Ltd.

2.2 Composite Fibers Preparation

2.2.1 Spinning Dope Preparation

Firstly, cellulose was isolated by alkali treatment of mulberry branch bark, then a fraction were hydrolyzed using 64 wt% of sulfuric acid solution for 30 min at 60 ℃ to prepare cellulose nanowhisker colloidal suspension as described previously [18].

Thereafter, 4 g of cellulose was dispersed in 100 g of NaOH/urea (7 wt%/12 wt%) aqueous solution pre-cooled at −10 ℃, then stirred vigorously for 10 min at room temperature to obtain a transparent solution, following the procedure demonstrated by Cai et al. [19]. Then the spinning dope with solid content of 3.5 wt% was prepared by adding the desired content of CNWs, in which