



# Modified treatment for carbonized cellulose nanofiber application in composites



Libo Ma<sup>a,b,c</sup>, Yang Zhang<sup>a</sup>, Siqun Wang<sup>c,\*</sup>

<sup>a</sup> College of Materials Science and Engineering, Nanjing Forestry University, Nanjing 210037, China

<sup>b</sup> Department of Chemistry and Materials Engineering, Changzhou Vocational Institute of Engineering Technology, Changzhou 213164, China

<sup>c</sup> Center for Renewable Carbon, University of Tennessee, Knoxville, TN 37996, USA

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## ABSTRACT

In the present study, carbon nanofibers (CNF) from carbonized cellulose nanofibers (CCNF) were prepared by carbonizing freeze-dried cellulose nanofibers first, then preparing acrylonitrile-butadienestyrene (ABS)/CCNF nanocomposites by extruder. To increase the dispersibility and operability of the CCNF, the ultrasound-assisted master batch method was adopted to make an ABS/CCNF master batch. Dicumyl peroxide and maleic anhydride were added to increase the interface compatibility between the CCNF and the ABS by reactive extrusion. The surface morphology, chemical structure, and mechanical properties of the ABS/CCNF nanocomposites were characterized by SEM, FTIR, and DMA/tensile tests, respectively. The tensile strength of ABS/CCNF was improved 36% compared to that of ABS. The improved properties demonstrated that the approach used in this study has the potential to solve the bottleneck issues of mass producing and applying CNF in a green way.

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## 1. Introduction

Carbon nanofibers (CNF), usually have diameters from 50 to 200 nm and lengths from 50 to 100  $\mu\text{m}$ , with relatively high aspect ratios (length to diameter) [1]. CNF has excellent mechanical properties, including a tensile strength of 5 GPa and a tensile modulus of 500 GPa [2]. With these superior mechanical properties, CNF can be made into composites and is especially useful as reinforcement in the advanced composite materials that are widely used as mechanical structural materials for the aerospace, and automotive industries, in electrical appliances, and in military applications, among many others [3].

Catalytic vapor deposition (CVD) and electrospinning are two main methods of preparing CNFs. Using CVD, CNFs can be made from hydrocarbons decomposed by catalysis on small metal particles; CNFs made by this process are also called vapor-grown carbon fibers (VGCF). The diameter is controlled by the catalyst particles [4]. The catalyst includes iron, cobalt, nickel, chromium, and vanadium [5], and the carbon sources include molybdenum, methane, carbon monoxide, synthesis gas ( $\text{H}_2/\text{CO}$ ), ethyne or ethane [6]. However, this method is difficult when applied in mass production.

Electrospinning is another way to prepare CNFs. Electrospinning utilizes a high electric field to charge the polymer solution; then the fibers can be drawn from the nozzle. First, high-purity polymer solution must be prepared to avoid blocking the nozzle, and the most organic solvents are consumed when preparing the polymer solution. After electrospinning is established, polymer nanofibers come into the carbonization process to form CNFs. Although many polymers can be electrospun to form polymer nanofibers, such as polyacrylonitrile (PAN), pitches, polyvinyl acetate (PVA), and polyvinylidene fluoride (PVDF) [7], the numbers of polymer nanofibers which can be transformed into carbon nanofibers are rather limited. Moreover, due to various complicating factors, such as the properties of the different polymer solutions, processing conditions, and atmospheric conditions, it is difficult to establish universal parameters for producing carbon nanofibers through electrospinning [7]. Another difficulty is that commercial carbon fibers are mainly produced by carbonizing organic fibers, of which polyacrylonitrile (PAN) is the first choice as the precursor because of its good mechanical property [8]. However, PAN is a petroleum-based polymer and thus may not always be available in the future as a nonrenewable resource. Today, interest in preparing carbonaceous materials from biomass materials is growing because biomass is abundant, low-cost, renewable, and comparatively environmentally benign. Therefore, the search for non-petroleum-based and sustainable precursors for CNF production responds to several pressing needs.

\* Corresponding author.

E-mail address: [swang@utk.edu](mailto:swang@utk.edu) (S. Wang).

Cellulose is one of earth's most abundant, renewable, environment friendly materials, and has been studied as the substance of many functional materials [9–14]. With diameters smaller than 100 nm, cellulose nanofibers have special properties; in particular, their outstanding mechanical properties, such as moduli up to 140 GPa, approaching the mechanical properties of steel (200 GPa) [15]. The preparation of cellulose nanofiber and its application in the production of composites has been widely studied [15–18]. Due to its nanoscale morphology, high carbon content and wide variety of available sources, cellulose nanofiber maybe an intriguing precursor for CNF production by carbonization [19]. Although CNF can be obtained by electrospinning solution of cellulose [20], preserving the nanofibrous structure of cellulose nanofiber during carbonization is a challenge due to the existence of many hydroxyl groups within the cellulose nanofibers. If there is not sufficient distance between the cellulose nanofibers, chemical bonds can easily form during carbonization, rendering the mechanical properties inferior [15,21,22]. In recent years, several groups have found that freeze-drying cellulose nanofiber is a suitable way to prepare CNF [21–24], because it can keep the nanofibrous structure intact during carbonization. In contrast to CVD and the electrospinning method, there are no catalysts or chemical solvents used during the freeze-drying and carbonization of the cellulose nanofiber. Therefore, the freeze-dried cellulose nanofiber not only can provide renewable material but also is a greener source for preparing CNF.

CNFs have been studied as reinforcement in polymer composites, such as PA-12 [25], PET [26], vinyl ester [27], PMMA [28], epoxy [29,30], and others. Although CNFs have a large specific surface area/aspect ratio and good mechanical properties, the reinforcing effect of CNF in composite is not as dramatic as might be expected. The reasons include the difficulty of dispersing CNFs evenly, the alignment of the fibers, and poor interface adhesiveness between the nanofibers and the matrix, which decreases the load transfer at the interface. In addition, CNFs, if used directly in industry workshops, would pose danger to workers because most nanomaterials are so fluffy that they can enter the lungs of the workers, causing inflammation and possibly creating fibrous growths in the lungs [31]. Thus, the drawbacks of using CNFs in composites seriously restrict their industrial uses spurring the continuing search for a feasible, low-cost and environmentally friendly way to mass-produce CNFs for use as reinforcement in composites.

Ultrasound-assisted master batch method (UMB) is an improved master batch technique that uses the power of ultrasound to help the nanofiller separate and disperse evenly within the polymer matrix; it is especially suitable for separating agglomerated nanofillers [32]. Moreover, using the master batch method allows the nanofiller to be applied within the matrix at a higher concentration, improving the operational safety of the nanofillers, as has been reported by our group [33]. In addition, surface modification of CNFs is also important due to the normally poor compatibility between CNFs and the matrix. Reactive extrusion is always carried out in an extruder, which encourages the generation of new chemical bonds through a melt phase reaction [34,35]. Just as usefully, reactive extrusion is an effective method to improve the compatibility between CNF filler and the matrix [36,37].

Acrylonitrile-butadiene-styrene (ABS) is a thermal plastic that is widely used due to its excellent mechanical properties, high dimensional stability, facility of processing, fine surface appearance, and relatively low price compared to other high performance plastics such as nylons. To enhance the mechanical properties of ABS and to enlarge its fields of application field, carbon nanofiber can be introduced into ABS to make the composites [38,39]. However, to date, there has appeared almost no information about preparing ABS/CNF composites in which CNF has been carbonized from cellulose nanofiber.

In the present study, carbon nanofibers from carbonized cellulose nanofibers (CCNF) were prepared by carbonizing freeze-dried CNFs first, then preparing ABS/CCNF nanocomposites by extruder, as noted, a commonly used method in the polymer processing industry. To increase the dispersibility and operability of the CCNF, the ultrasound-assisted master batch method was adopted to make an ABS/CCNF master batch. Dicumyl peroxide (DCP) and maleic anhydride (MAH) were added to increase the interface compatibility between the CCNF and the ABS by reactive extrusion. The surface morphology, chemical structure, and mechanical properties of the ABS/CCNF nanocomposite were characterized by SEM, FTIR, and DMA/tensile tests, respectively. In contrast to the traditional approach of preparing CNF, here we used cellulose nanofiber, a renewable material, as the precursor of the CNF, an approach that has the potential to solve the bottleneck issues of mass producing and applying CNF in a green way.

## 2. Experimental

### 2.1. Materials

Cellulose nanofiber in water suspension was purchased (University of Maine, USA), with a solids content of 2.95 wt%. Acrylonitrile-butadiene-styrene (ABS) was purchased in China (Ningbo Taihua AG15A1). Maleic anhydride (MAH) and dicumyl peroxide (DCP) were purchased from Sigma Aldrich Co. Ltd. Paraffin emulsion (Cascowax EW-58LV, Momentive Specialty Chemicals Inc., USA) and acetone (Klean-Strip 1-gal, Model<sup>#</sup> GAC18, USA) were purchased as well.

### 2.2. Preparing CCNF from cellulose nanofiber

First, diluted cellulose nanofiber (from 2.95 wt% to 2 wt%) solution was sealed in copper tubes and dipped into liquid nitrogen for 3–5 min; then the frozen cellulose nanofiber was freeze-dried in a vacuum lyophilizer (Labconco, Inc., Kansas City, MO) at a temperature of  $-51^{\circ}\text{C}$  for 72 h. An ultra-light sponge-like cellulose aerogel was obtained.

The cellulose aerogel was carbonized using a Lindberg/blue M Mini-Mite tube furnace (Thermo Scientific). First, the cellulose aerogel was stabilized from room temperature to  $320^{\circ}\text{C}$  at the rate of  $2^{\circ}\text{C}/\text{min}$  under air. Second, the temperature was increased from  $320^{\circ}\text{C}$  to  $1000^{\circ}\text{C}$  at the rate of  $5^{\circ}\text{C}/\text{min}$  under nitrogen gas and held for 60 min at  $1000^{\circ}\text{C}$ . Finally, samples were cooled to room temperature, and an ultra-light sponge-like carbon aerogel was obtained.

### 2.3. Preparing ABS/CCNF composites with different methods

The UMB method was adopted to prepare the CCNF master batch. First, carbon aerogel was subjected to ultrasound (Vibra-Cell, Model VCF-1500) under acetone solvent for 30 min to obtain the CCNF suspension. The ABS used in this study was first dried at  $60^{\circ}\text{C}$  for 6 h in an oven to reduce the moisture content to less than 1%. Secondly, ABS/acetone (10 wt%) solvent and paraffin emulsion were added into the CCNF suspension and also ultrasound-treated for 30 min. Paraffin was used as the dispersing agent in the master batch. The weight ratio (ABS:CCNF:paraffin) was (55:40:5). Third, the mixed solution was magnetically stirred under the chemical hood to make the acetone evaporate. A master batch with a high content of CCNF (40 wt%) was obtained for future use.

ABS/CCNF nanocomposites were prepared according to different methods, and the main differences were shown in Table 1. To prepare sample #1, CCNF aerogel was crushed in a kitchen blender to get CCNF powder. Then ABS and CCNF powder (1 wt%) via a two-

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