Materials Letters 109 (2013) 175–178

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Porous core-shell carbon fibers derived from lignin and cellulose nanofibrils

Xuezhu Xu [a,b], Jian Zhou [b], Long Jiang [a,*], Gilles Lubineau [b,**], Ye Chen [c], Xiang-Fa Wu [a], Robert Piere [a]

[a] Department of Mechanical Engineering, Program of Materials and Nanotechnology, North Dakota State University, P.O. Box 6050, Fargo, ND 58108, United States
[b] King Abdullah University of Science and Technology (KAUST), Physical Science and Engineering Division, COHMAS Laboratory, Thuwal 23955-6900, Saudi Arabia
[c] King Abdullah University of Science and Technology (KAUST), Physical Science and Engineering Division, CRD Laboratory, Thuwal 23955-6900, Saudi Arabia

ARTICLE INFO

Article history:
Received 16 May 2013
Accepted 20 July 2013
Available online 26 July 2013

Keywords:
Lignin
Polyacrylonitrile (PAN)
Electrospinning
Carbon fiber
Cellulose nanofibrils (CNFs)

ABSTRACT

This letter reports a method to produce lignin and cellulose nanofibrils (CNFs) based porous core-shell carbon fibers via co-electrospinning followed by controlled carbonization. Lignin formed the shell of the fiber while CNF network formed the porous core. Polyacrylonitrile (PAN) was added to the lignin solution to increase its electrospinability. CNFs were surface acetylated and dispersed in silicon oil to obtain a homogenous dispersion for electrospinning the porous core. Hollow lignin fibers were also electrospun using glycerin as the core material. FT-IR measurements confirmed the CNF acetylation. SEM micrographs showed the core-shell and hollow fiber nanostructures before and after carbonization. The novel carbon fibers synthesized in this study exhibited increased surface area and porosity that are promising for many advanced applications.

1. Introduction

Carbon nanofibers have received tremendous research interest because of their great potential in energy, chemical sensing and adsorption, and catalysis applications. Synthesis of carbon nanofibers based on renewable materials represents a relatively new but high-impact research direction with obvious environmental benefits. Lignin and cellulose are two most abundant natural polymers and have been shown to be effective carbon precursors. Submicron diameter carbon fibers has been produced by carbonizing electrospun lignin fibers [1]. Natural cellulose fibers have been converted into carbon fibers through controlled pyrolysis and the effects of the pyrolysis conditions on the conversion and the properties of the obtained carbon fibers have been studied [2–4]. CNFs are one type of cellulose nanofibers that have very large aspect ratio and form percolated network structures in water or polymer matrices. They have been under intensive investigation for use as potential biobased nanoreinforcements in polymer nanocomposites [5].

The performance of carbon nanofibers in many applications depends on their surface areas. Hollow fibers, [6] porous fibers [7] and fibers with carbon nanotubes grown on the fiber surface [8] have been developed to increase the surface area. In this letter, we reported the preparation of core-shell carbon fibers via electrospinning biobased precursors followed by controlled carbonization. Lignin was used as the spinning material for the shell part of the fiber while a portion of PAN was added to increase its spinnability. CNFs were used to form the porous core structure of the fiber. The obtained core-shell carbon fibers exhibited increased surface area which is expected to improve their performance in many advanced applications.

2. Materials, preparations and characterizations

Materials: Alkali kraft lignin and PAN with an average Mw of 150,000 were purchased from Sigma-Aldrich. Cellulose nanofibril gel (2.3 wt%) produced by repeated mechanical grinding [9] was kindly provided by USDA Forest Products Laboratory (Madison, WI). N,N-Dimethylformamide (DMF) (≥99.8%), chloroform (≥99.8%), glacial acetic acid (≥99.7%), sulfuric acid (95.0–98.0%), acetic anhydride (≥97%), and poly(dimethylsiloxane) (96%) were purchased from Fisher Scientific. Ethyl alcohol (EtOH, 100%) was purchased from VWR. All chemicals are used as received without further purification.

Preparation of acetylated CNFs/silicone oil suspension: CNFs were dispersed in DMF through solvent exchange before acetylation

* Corresponding author. Tel.: +1 701 231 9512.
** Corresponding author. Tel.: +966 02 808 2983.
E-mail addresses: long.jiang@ndsu.edu (L. Jiang), gilles.lubineau@kaust.edu.sa (G. Lubineau).

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http://dx.doi.org/10.1016/j.matlet.2013.07.082

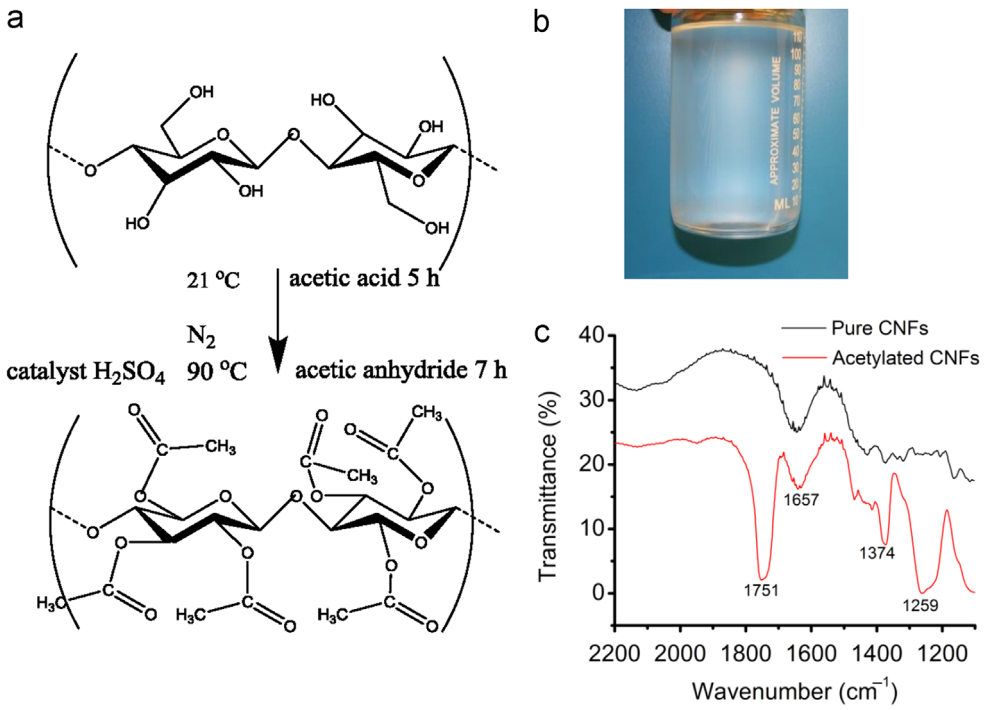

Fig. 1. (a) Reaction scheme of CNF acetylation; (b) acetylated CNFs dispersed in a silicone oil/chloroform mixture (~0.5 wt%) and (c) FT-IR spectra of pure CNFs and surface modified CNFs.

reaction. 100 mL DMF was gradually added into 43.48 g CNF gel (1 g dry CNFs) under continuous stirring at 100 °C. 50 g white gel-like CNF/DMF suspension (2 wt%) was obtained after ~3– h stirring. Acetylation was conducted in a three-neck round flask under N_2 protection. 40 mL acetic acid and 2 mL sulfuric acid were added into the 50 g CNF/DMF suspension at room temperature to activate the CNF surfaces (5 h). Then 40 mL acetic anhydride was added to trigger the acetylation. The reaction lasted 7 h at 90 °C under continuous stirring. The reaction product was transferred to a 2,000 mL narrow-neck flask and then 1,000 mL EtOH was added afterward. The mixture was stirred at room temperature for over 30 h. The precipitate (i.e., acetylated CNFs) of the mixture was collected and unreacted chemicals were removed by repeated centrifugation (Eppendorf centrifuge 5810, 4,000 rpm for 2 min). The acetylated CNFs were dispersed in 60 mL silicone oil (90 °C) using a high speed homogenizer (IKA T18 basic) at ~500 rpm until the mixture became transparent (about 1 h). 10 mL chloroform was added into the suspension to further increase the dispersion of the acetylated CNFs. Finally, a homogenous acetylated CNFs/silicone oil/chloroform mixture was obtained which remained stable over 24 h.

Electrospinning and fiber carbonization: Lignin and PAN were dissolved in DMF by stirring overnight at 60 °C. The ratio between lignin and PAN was 1:1 and the total solid content of the solution was 17 wt%. The obtained solution was used to spin the shell part of the core-shell fibers while the acetylated CNF/silicone oil/chloroform mixture was used for the core part. Electrospinning was conducted on an EC-DIG electrospinning apparatus (IME Technologies, Netherlands) equipped with a co-axial spinneret with the inner and outer gauges being 19 and 15, respectively. A voltage of 17 kV was applied between the needle and the fiber collector (grounded). The feeding rates of the core and shell materials were adjusted to 0.03 mL/h. The distance between the needle tip and the collector was kept at ~20 cm. Pure glycerin was used for the core material when hollow lignin/PAN fiber was produced. All spinning processes were performed under a relative humidity of 63% at 21 °C.

The obtained fibers were carbonized in a home-made horizontal tubular furnace. The temperature of the furnace was first increased from 21 to 550 °C at 10 °C/min and maintained for 2 h in a mixture atmosphere of 500 ml/min hydrogen (H_2) and 1 ml/min argon (Ar). Then the temperature was increased to 1000 °C at 10 °C/min and maintained for 1 h in 500 ml/min Ar to fulfill the carbonization process.

Characterizations: Scanning electron microscope (SEM) imaging was performed on a Quanta 3D FEG (FEI) operating at 10 kV. Cross-sections of the electrospun nanofibers were obtained by first dipping the fibers in liquid nitrogen followed by a clean cut using a razor blade. Carbonized nanofibers were directly cut without the cryo-treatment. Before imaging, the samples were coated with a thin layer of Au using an Emitech K575X sputter coater. FT-IR spectra were obtained on a Nicolet iS10 from Thermo Fisher Scientific Inc. The fiber samples were ground with KBr (ratio 1:100) and molded into discs. The spectrum between 4,000 and 500 cm^{-1} was collected for each sample based on 32 scans with a resolution of 4 cm^{-1}. The spectra were processed and analyzed using OMNIC 8.1 (Thermo Scientific). Background reference was obtained by scanning a pure KBr disc under the same condition.

3. Results and discussion

CNFs were acetylated because they could not be homogeneously dispersed in non-polar silicon oil due to their high surface polarity. This high polarity can be greatly decreased by acetylation. The reaction scheme of CNF surface acetylation is shown in Fig. 1a. The active hydroxyl groups (-OH) on the surfaces of CNFs react with acetic acid or acetic anhydrate to produce acetyl groups (-$COCH_3$) [10]. The acetylation of CNFs lowers their hydrophilicity and thus improves their dispersion in non-polar solvents such as silicon oil. The stability of the acetylated CNF dispersion can be further improved by adding chloroform into silicon oil due to the similarity between the polarity of the acetylated CNFs and chloroform [10]. The suspension remained stable over 72 h. In Fig. 1(b),