



Stabilization kinetics of gel spun polyacrylonitrile/lignin blend fiber

H. Clive Liu^{a, b}, An-Ting Chien^a, Bradley A. Newcomb^a, Amir A. Bakhtiary Davijani^a, Satish Kumar^{a, b, *}



^a School of Materials Science and Engineering, Georgia Institute of Technology, 801 Ferst Drive NW, MRDC-1, Atlanta, GA 30332, United States

^b Renewable Bioproducts Institute, Georgia Institute of Technology, 500 10th Street NW, Atlanta, GA 30332, United States

ARTICLE INFO

Article history:

Received 2 October 2015

Received in revised form

25 January 2016

Accepted 29 January 2016

Available online 1 February 2016

ABSTRACT

Composite fibers from polyacrylonitrile (PAN) and softwood lignin (SWL) were successfully fabricated to investigate the effects of lignin on fiber properties and thermal stabilization reaction kinetics. PAN/SWL composite precursor fiber exhibits comparable tensile properties to PAN fiber. This is attributed to the antiplasticization effect of lignin on PAN. Thermal stabilization reactions (e.g. oxidation, cyclization, and crosslinking) for both PAN and PAN/SWL fibers were individually studied by different scanning calorimetry. The addition of SWL was shown to reduce the activation energies and increase reaction rates of cyclization, oxidation and crosslinking. Thermo-mechanical analysis (TMA) was employed to monitor the effect of applied tensions on PAN cyclization kinetics under non-isothermal heating process. Cyclization activation energies of PAN/SWL fiber are shown to be consistently lower than those of PAN fiber under all applied tensions. Calculations of cyclization reaction kinetics constants from TMA indicate that SWL can promote PAN cyclization and crosslinking.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Throughout the development and increasing demand of carbon fibers, polyacrylonitrile (PAN) has been the predominant precursor for the production of high performance carbon fibers and these accounts for more than 90% of the commercial carbon fibers [1]. Owing to the relatively high cost, applications of carbon fibers are rather limited [1]. While significant cost reductions have been achieved in carbon fiber production over the last three decades, further cost reductions will significantly increase carbon fiber usage, especially in the automotive sector. Current market demand for low-cost carbon fiber is approximately 300 million kg per year [2]. As one of the most abundant renewable materials on earth and the byproduct of pulp and paper industry, lignin has been considered an attractive cost-effective alternative to PAN for carbon fiber precursors [3]. To-date, lignin based carbon fibers have exhibited relatively low mechanical properties compared to the PAN based carbon fibers [4,5]. Although numerous efforts have been devoted to lignin derived carbon fibers since 1960s [6–11], understanding of

the fundamental chemistry of this process is still limited and requires further development in translational biorefinery research [2,12].

Over the last decade, there has been interest, in both academic and industrial laboratories [13–18], to integrate the cost advantages of lignin and the good mechanical properties of PAN. As a result, PAN/lignin blend based carbon fibers have been processed with comparable mechanical performance to that of the control PAN based carbon fibers [19]. In one of the reports, it has been suggested that the incorporation of lignin could potentially increase PAN stabilization efficiency [20]. In two separate studies it was suggested that lignin incorporation could initiate PAN stabilization process at a relatively low temperature [19,21]. However, no details regarding the reaction mechanisms and kinetics were discussed in these studies. Therefore, in this study we report for the first time, the stabilization reaction kinetics of gel spun PAN/lignin blend fibers.

2. Experimental

2.1. Materials and fiber processing

PAN-co-MAA (96/4, $M_v = 247,000$ g/mol) was acquired from Exlan, Co. (Japan). Softwood kraft lignin (Indulin AT) was provided

* Corresponding author. School of Materials Science and Engineering, Georgia Institute of Technology, 801 Ferst Drive NW, MRDC-1, Atlanta, GA 30332, United States.

E-mail address: Satish.Kumar@mse.gatech.edu (S. Kumar).

by MeadWestvaco (Richmond, VA). Kraft lignin typically has relatively high (typically higher than 2 wt%) sulfur content [22,23]. For comparison, we note that in our previous work [19], annual plant lignin with soda pulping process was used and that lignin contained about 0.5 wt% sulfur [24]. As-received lignin powder was first treated with diluted HCl and distilled water repeatedly, followed by multiple washes with methanol to filter the insoluble fraction. Methanol-treated lignin was then washed with distilled water repeatedly and dried under vacuum at 60 °C overnight before use. Dimethylformamide (DMF) was obtained from Sigma–Aldrich Co. and used as received. For solution preparation, PAN and lignin solids are dissolved into DMF in a glass reactor maintained at 80 °C. PAN solution is prepared at a solid concentration of 15 g/dL. When preparing for PAN/lignin solution, 5 g/dL of lignin solid was dissolved in DMF while PAN solid concentration remained unchanged. (PAN:lignin solid content ratio = 75:25.) A spinning system designed by Hills, Inc. and a spinnerette with a 200 µm diameter hole were used for fiber spinning. Fibers were spun through an air gap of 30 mm into a methanol coagulation bath maintained at −50 °C. As-spun fibers were collected at a spin draw ratio of 3 and subsequently kept immersed in methanol at −30 °C for 36 h to ensure gelation before further fiber drawing. Post-spin fiber drawing was first performed in ambient condition and later in a glycerol bath maintained at 165 °C. All fibers in the current study were drawn to a total draw ratio of 10, and the diameter of PAN and PAN/softwood kraft lignin (SWL) fibers were 21.7 µm and 21.2 µm, respectively.

2.2. Characterization

Dynamic mechanical analysis (DMA) was performed on precursor fibers at a frequency of 1 Hz using a RSA III solid analyzer. 30-filament fiber bundles were used at a gage length of 25.4 mm at a heating rate of 1 °C/min from 30 °C to 200 °C. Tensile properties of precursor fibers were tested via FAVIMAT on single filaments at 25.4 mm gage length and at a strain rate of 1%/s. At least 20 fibers were tested in each case. Scanning electron microscope (SEM) images of the fibers were collected using Zeiss Ultra 60 FE-SEM at an accelerating voltage of 5 kV. Fourier transform infrared spectra (FTIR) of SWL powder, PAN fiber and PAN/SWL fiber are collected on Spectrum One from PerkinElmer with a resolution of 1 cm^{−1}. To study the fiber structure, Wide angle X-ray diffraction (WAXD) patterns were obtained by Rigaku Micromax-002 and Rigaku IV++ detecting system with operating parameters of 45 kV, 0.65 mA and $\lambda = 1.5418$ Å. Softwares AreaMax V1.00 and MDI Jade 6.1 were used to analyze the WAXD patterns. Thermo-mechanical analysis (TMA Q400, TA Instruments) was conducted with 10-filament fiber bundles at various applied stresses and heating rates (1, 3, and 5 °C/min) to 325 °C under nitrogen and air environment. Differential scanning calorimetry (TA Instrument Q2000) under oxidative and nitrogen environments at various heating rates (5, 10, and 15 °C/min) from 25 °C to 400 °C were performed on fibers in order to differentiate stabilization reactions.

3. Results and discussion

Mechanical properties and structural parameters of precursor fibers are summarized in Table 1, and the SEM images of the tensile fractured fiber surfaces are shown in Fig. S1. The tensile properties of the PAN and PAN/SWL fibers are comparable to each other. PAN/SWL fiber has a lower PAN crystal size than PAN fiber and similar PAN crystal orientation. Storage modulus and $\tan \delta$ curves along with the loss modulus of the fibers from DMA are shown in Fig. 1. The PAN $\tan \delta$ peak at ~90 °C is attributed to β_c relaxation of the polymer chain motion in the para-crystalline region [25]. In the

Table 1
Mechanical properties and structural parameters of precursor fibers.

	PAN	PAN/SWL
Tensile modulus (GPa)	14.7 ± 0.8	16.0 ± 0.6
Tensile strength (MPa)	624 ± 61	776 ± 50
Strain to failure (%)	8.7 ± 0.5	8.6 ± 0.4
Fracture toughness (MPa)	31.3 ± 3.0	37.2 ± 4.8
f_{PAN}^a	0.82	0.82
Crystal size ^b (nm)	11.8	9.3
$d_{2\theta \approx 17^\circ}^c$ (Å)	5.243	5.263
$d_{2\theta \approx 30^\circ}^d$ (Å)	3.031	3.045
$2\theta_{\text{meridional scan}}^e$ (°)	39.14	39.13

^a Herman's orientation factor of PAN, calculated from Azimuthal scan of PAN (2 0 0), (1 1 0) planes.

^b The crystal size of PAN calculated using WAXD peak at $2\theta \approx 17^\circ$.

^c Equatorial PAN d-spacing. (for $2\theta \sim 17^\circ$ diffraction peak).

^d Equatorial PAN d-spacing. (for $2\theta \sim 30^\circ$ diffraction peak).

^e PAN peak position from meridional scan.

current study, PAN and PAN/SWL fiber exhibited relatively unchanged meridional peak positions obtained from WAXD (Table 1), suggesting that there was no significant effect on polymer chain conformation by incorporating SWL in the fiber. Interestingly, DMA of PAN/SWL fiber shows a noticeably reduced $\tan \delta$ peak magnitude (Fig. 1a) and a diminished shoulder on loss modulus curve ~90 °C (Fig. 1b) as compared to the PAN fiber, implying a suppressed β_c relaxation that can result from anti-plasticization effect [26–30]. While antiplasticization effect is critically dependent on the additive species [30], it is interesting that antiplasticization is observed between pre-treated softwood lignin and PAN copolymer in the current study, but not in the previous study of acid-treated annual plant lignin and homo-polymer PAN [19].

Thermal stabilization is a critical processing stage during PAN based carbon fiber manufacturing [5,31,32]. During stabilization, PAN fibers undergo complex reactions including oxidation, cyclization, and crosslinking that transform PAN polymer chains into stabilized ladder polymer structure [33–35]. While the cyclization reaction can be initiated with or without the presence of oxygen, oxidation and crosslinking can only occur under an oxidative environment [36]. This allows separation and monitoring of the individual stabilization reactions under inert or oxidative environments by differential scanning calorimetry (DSC) [37–39]. When the PAN fiber was stabilized under an oxidative condition, a broad exothermic peak constituted by multiple peaks from concurrent reactions were observed as Fig. 2a. When the PAN fiber was run in a nitrogen environment, a single narrower peak corresponding to the cyclization reaction appeared as shown in Fig. 2b [38]. While quickly quenched the sample from nitrogen run back to room temperature followed by a rerun in an oxidative environment by DSC, two broad peaks were then evolved (Fig. 2c). These peaks were assigned to oxidation and crosslinking reactions [40].

To analyze the effects of lignin on stabilization reactions and kinetics by DSC, PAN and PAN/SWL fibers were run in nitrogen first and then rerun in air with heating rates of 5, 10, and 15 °C/min (Fig. 3). In heat treatments under nitrogen, a single exothermic peak was observed from both PAN and PAN/SWL fibers, attributed to the cyclization reaction. Shown as Fig. 3a and b, PAN/SWL fibers exhibited lower exothermic heat flow magnitude than PAN fiber. Fast heat release during the reaction could result in local overheating [39], and the incorporation of lignin can alleviate excessive heat release during cyclization.

To further investigate reaction activation energies and reaction kinetics from DSC, peak temperatures of cyclization (in nitrogen), oxidation (in air), and crosslinking (in air) were collected and listed in Table 2 for calculations by the Kissinger method (eq. (1)) and Ozawa method (eq. (2)), where ϕ , T_p , E_a , R are heating rate (°C/min),

Download English Version:

<https://daneshyari.com/en/article/1413280>

Download Persian Version:

<https://daneshyari.com/article/1413280>

[Daneshyari.com](https://daneshyari.com)