



# Reinforcement of lignin-based carbon fibers with functionalized carbon nanotubes



Shichao Wang, Zhe Zhou \*\*, Hengxue Xiang, Wei Chen, Erqiang Yin, Tienkiang Chang, Meifang Zhu \*

State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, China

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## ABSTRACT

In an effort to increase the mechanical properties of lignin-based carbon fibers, carbon nanotubes grafted with lignin (CNTs-g-L) were synthesized by grafting lignin molecular chains onto the surface of CNTs to improve the interfacial adhesion between CNTs and lignin chains. The addition of CNTs-g-L improved the melt spinnability of lignin, and continuously spooled Lignin/CNTs-g-L melt spun fibers and their carbonized fibers were obtained. The interaction between CNTs-g-L and lignin phases improved the thermal stability of lignin but disordered the graphitic structure of lignin-based carbon fibers. The well-orientated CNTs-g-L increased the tensile strength of lignin-based carbon fibers from 171.2 MPa to 289.3 MPa when 0.5% CNTs-g-L was incorporated. However, due to voids generated by the breakage of chemical links in the functionalized CNTs, the tensile strength of carbon fibers obtained thus decreased with further increases in the CNTs-g-L content.

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## 1. Introduction

Lignin is an amorphous complex biopolymer with a heterogeneous structure derived mainly from *p*-coumaryl, coniferyl, and sinapyl alcohols [1]. As the only large-volume renewable feedstock composed of aromatics, lignin is considered the most attractive sustainable precursor for carbonaceous materials [2]. Among all carbonaceous materials, carbon fibers draw the most attention due to their high tensile strength and modulus. Currently, carbon fibers are mainly obtained from petroleum-based poly(acrylonitrile) (PAN) feedstock by a solution spinning method. High costs and environmental concerns restrict their further application in many fields, especially in the automotive industry [3]. Compared with PAN-based carbon fibers, lignin-based carbon fibers prepared from melt spinning show an unparalleled advantage in production costs and environmental concerns. However, poor melt spinnability and low mechanical properties hinder the development and application of lignin-based carbon fibers.

To solve the aforementioned bottlenecks, huge efforts have been

focused on the improvement of the melt spinnability of lignin because fine precursors are necessary for the manufacture of carbon fibers. A conventional method of improving the spinnability of lignin is chemical modification, including acetylation [4], esterification [5], etherification [6] and graft polymerization [7]. Although the meltability can be improved to a certain extent, the spinnability is still far from satisfactory. Moreover, the cost of modification is relatively high, which is not suitable for the large-scale production of carbon fibers. Another inexpensive method that can be applicable for industrial production is the blending of lignin with other melt-spinnable synthetic polymers. Poly(ethylene terephthalate) (PET), polypropylene (PP), poly(ethylene oxide) (PEO), and poly(lactic acid) (PLA) are used to facilitate the melt spinning process of lignin [3,8–10]. Continuously spooled lignin/polymer fibers are obtained by melt spinning. However, synthetic polymers will degrade and generate voids in the fibers during the stabilization and carbonization processes, leading to poor mechanical properties of the carbon fibers.

By contrast, very few studies have focused on increasing the mechanical properties of lignin-based carbon fibers directly. In recent years, carbon nanotubes (CNTs) with high tensile strength and tensile modulus have been successfully applied to improve the mechanical properties of precursors and carbon fibers. Chae et al. [11] studied the stabilization and carbonization of gel spun PAN/

\* Corresponding author.

\*\* Corresponding author.

E-mail addresses: [zzhe@dhu.edu.cn](mailto:zzhe@dhu.edu.cn) (Z. Zhou), [zhumf@dhu.edu.cn](mailto:zhumf@dhu.edu.cn) (M. Zhu).

CNTs fibers and reported that the addition of 1 wt% CNTs enhanced the carbon fiber modulus by 49% and the strength by 64%. More recently, CNTs have also been introduced into the lignin phase to prepare lignin/CNT-based carbon fibers. Teng et al. [12] prepared electrospun softwood kraft lignin/CNT fibers and their carbonized products, with results showing that the tensile strength and modulus of carbonized lignin/CNT/PEO were lower than those of lignin/PEO carbon fiber mats in all cases, which was attributed to the poor interfacial interaction between CNTs and the surrounding matrix. Liu et al. [13] in their recent work also demonstrated that the addition of CNTs to PAN/lignin composites decreased the tensile strength and modulus of PAN/lignin-based carbon fibers. As in the case of electrospinning and gel spinning, a poor increase in mechanical properties was also found in melt spun lignin/CNT fibers. Although no original data were provided, Baker et al. [14] reported that at an optimal level of CNTs, the lignin/CNT-based carbon fibers exhibited only a 20% increase in tensile strength compared to that of neat lignin-based carbon fibers. The reason for this poor increase was also attributed to the low interfacial adhesion between non-functionalized CNTs and lignin carbons.

To improve the interfacial adhesion, CNTs were modified by grafting, a simple and powerful way of forming a continuous interphase between CNTs and the matrix [15,16]. In the present work, we designed the compatibilizer by grafting lignin chains onto the surface of CNTs (abbreviated as CNTs-g-L). Continuously spooled lignin/CNTs-g-L fibers were prepared by melt spinning. The interaction between CNTs-g-L and lignin, the morphology, and the mechanical properties of the obtained carbon fibers were investigated to obtain comprehensive knowledge of the preparation of lignin-based carbon fibers enhanced by a carbon material.

## 2. Experimental section

### 2.1. Materials

Hardwood kraft lignin ( $M_w = 4610$ ,  $M_n = 3320$ ) was kindly provided by Suzano Papel e Celulose S.A. Corp., Brazil. Lignin was purified using a ceramic membrane with a cut-off value of 0.05  $\mu\text{m}$ , as described in our former work [3]. Industrial grade carboxyl multi-wall carbon nanotubes (–COOH content: 1.55%) were supplied by Chengdu Organic Chemicals Co. Ltd. (Chengdu, China). Methylene-diphenyl diisocyanate (MDI), chloroform ( $\text{CHCl}_3$ ), and dibutyltin dilaurate were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and used without further purification.

### 2.2. Synthesis of CNTs-g-L

The synthesis scheme of CNTs-g-L is illustrated in Fig. S1. Five grams of CNTs was swelled in 500 mL  $\text{CHCl}_3$  in a four-necked round-bottom flask and sonicated for 40 min in an oil bath (50 °C). Two milliliters of MDI was added to the flask with continuous mechanical stirring for 1 h under a nitrogen atmosphere. After that, 3 g of purified lignin and two drops of catalyst (dibutyltin dilaurate) were added to the solution and reacted for another 3.5 h. The resulting solution was filtered and washed five times with  $\text{CHCl}_3$  to remove unreacted lignin and other reagents before being collected and dried at 80 °C under vacuum overnight. Then, the dry CNTs-g-L were Soxhlet extracted for 48 h using  $\text{CHCl}_3$  to remove adsorbed lignin before testing.

### 2.3. Preparation of lignin/CNTs-g-L fibers and their carbonized fibers

Lignin and CNTs-g-L powders were mixed together in an

internal mixer at 220 °C for 5 min at a roller speed of 50 rpm. The CNTs-g-L contents used were 0, 0.5, 1, 2 and 3 wt% of the total weight, and the corresponding composites were labeled as lignin, lignin/0.5%CNTs-g-L, lignin/1%CNTs-g-L, lignin/2%CNTs-g-L and lignin/3%CNTs-g-L, respectively. All of the lignin/CNTs-g-L composites were fed into a twin screw micro-compounder equipped with a take-up device and processed at 225 °C. The obtained fibers were adhered to a ceramic ark and carbonized according to our former work [3]. The characterization methods of Lignin/CNTs-g-L composites and their carbonized fibers were supplied in the supplementary information.

## 3. Results and discussion

### 3.1. Structural characterization of CNTs-g-L

A valuable tool for estimating the species and amounts of hydroxyl (OH) relies on  $^{31}\text{P}$  NMR analysis of lignin derivatized in situ by 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP) [17,18]. As shown in Fig. S2, aliphatic OH, syringyl (S) phenolic OH, guaiacyl (G) phenolic OH and carboxylic acid OH were seen in the purified lignin. The specific contents were calculated and are supplied in Table S1. Aliphatic OH and carboxylic OH from lignin and CNTs provided opportunities to react with NCO groups from carbon content-enriched MDI. To confirm our hypothesis, FTIR was used to elucidate the structural differences between unmodified CNTs and modified CNTs (Fig. 1). From Fig. 1(a), we can see that O–H stretching, C–H stretching and C=O stretching appeared in all of the spectra, although there are differences in their relative intensities. In contrast to CNTs, CNTs-g-L showed two remarkable peaks that appeared at 1512  $\text{cm}^{-1}$  and 1113  $\text{cm}^{-1}$ , which corresponded to functional groups in lignin (Fig. 1(b)). The appearance of a band at 1512  $\text{cm}^{-1}$  was assigned to the characteristic vibration of the aromatic skeleton, while the absorption at 1113  $\text{cm}^{-1}$  represented C–H stretching of the S ring and G ring [19]. In addition, the C–N stretching absorption was also found at 1402  $\text{cm}^{-1}$  in CNTs-g-L samples.

To further investigate the structure of CNTs-g-L, XPS was used to measure the near-surface composition and examine the valence states of the observed elements [20]. As shown in Fig. 2(a), the XPS spectrum of unmodified CNTs showed only the presence of carbon and oxygen atoms. However, nitrogen atoms were clearly found in the spectrum of CNTs-g-L (Fig. 2(c)), and the calculated N/C atomic ratio was 0.023. In addition, the O/C atomic ratio increased from 0.032 in CNTs to 0.129 in CNTs-g-L. Fig. 2(b) shows the high-resolution XPS spectra of C 1s of CNTs. The strong C 1s peak (284.7 eV) corresponded to graphitic carbon, while the weaker peaks were assigned to C–O (286.2 eV) and –C\* (292.6 eV). After modification, the peak intensity of 286.2 eV increased significantly (Fig. 2(d)), which was caused by the formation of C–N bonds and the contribution from C–O bonds that are present in high quantities in lignin. The results of FTIR and XPS demonstrate that lignin was successfully grafted onto the surface of CNTs.

### 3.2. Interaction between CNTs-g-L and lignin

The TG curves of CNTs, CNTs-g-L and their composites with lignin are shown in Fig. 3. The degradation parameters are summarized in Table 1, including the temperature at 5% weight loss ( $T_{5\%}$ ) and the residual weight at 1000 °C ( $W_f$ ). The weight loss of CNTs is due mainly to amorphous carbon and other impurities in CNTs [21]. Compared with unmodified CNTs, large mass loss in CNTs-g-L occurred when the temperature was above 260 °C because of the degradation of the propanoid side chains of lignin [22]. As a result, the  $T_{5\%}$  of lignin and CNTs-g-L occurred at 316.5 °C

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