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Preparation of low-cost carbon fiber precursors from blends of wheat straw lignin and commercial textile-grade polyacrylonitrile (PAN)

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Abstract: Low-cost precursor fibers (PFs) were prepared from blends of a wheat straw lignin (WSL) and a commercial textile-grade polyacrylonitrile (PAN) by wet spinning, and then the precursors were converted into carbon fibers (CFs) by thermal stabilization and carbonization. The PFs were characterized by scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC). The lignin content in the blends was found to play an important role in the PF structure, which was closely related to the change of intermolecular forces in the spinning solution. The lignin, acting as the carboxylic acid comonomer, had significantly promoted the thermal stabilization of the lignin/PAN blend PFs, which helped to further decrease the production cost of CFs. With increasing lignin contents, the carbon content of CFs remained at about 95%. The carbon of lignin could be utilized for the preparation of CFs.

Keywords: blend, carbon fiber, lignin, polyacrylonitrile, precursor, thermal stabilization, wet spinning

Introduction

Carbon fibers (CFs) have attracted attention worldwide as strong and lightweight reinforcement materials for fabricating advanced composites (Huang 2009). Currently, more than 90% of commercial CFs are produced from polyacrylonitrile (PAN). Due to their excellent mechanical properties, PAN-CFs have been widely applied in aviation, aerospace and high-end sporting goods industries (Xia et al. 2016). However, the high price of the petroleum-derived raw material and the high-cost production process have limited the applications of PAN-CFs in more common areas including automotive and construction industries (Foston et al. 2013).

The precursor fibers (PFs) contribute about half of the total cost of the conventional PAN-CFs (Warren et al. 2009). Therefore, lowering the cost of PF production is important and there are various ways to reach this goal. For example, the textile-grade PAN-PFs have been used for CF production (Yoo et al. 2017), new melt-spinnable PAN-PFs were synthesized (Miller et al. 2017) and polyolefin and lignin were converted to CFs (Chatterjee and Saito 2015). Among all these candidates, lignin is meaningful and of great importance, because it is an abundant carbon-rich renewable resource, available as a major by-product of the pulping industry (Wang et al. 2015). Technical lignins have recently attracted great attention as activated CFs for carbon yarn supercapacitors (Huang and Zhao 2016; Huang et al. 2018) or for multifunctional lithium-ion battery electrodes (Nowak et al. 2018).

Lignin is a complex amorphous polymer with a cross-linked network structure (Ye et al. 2017), which results in poor spinnability. The development of continuous lignin PFs is a great challenge (Mainka et al. 2015) and various methods have been proposed to this purpose (Youe et al. 2016; Park et al. 2017). A usual approach is to blend lignin with other polymers with good spinnability. Some thermoplastic polymers, such as poly(ethylene oxide) (PEO), poly(ethylene terephthalate) (PET), polypropylene (PP) and poly(lactic acid) (PLA), were tested to prepare lignin PFs by melt spinning (Ragauskas et al. 2014). However, the poor

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thermal stability and poor miscibility of these polymers led to unacceptable mechanical properties of the CFs.

PAN is also a good candidate for blending with lignin to prepare PFs (Seydibeyoglu 2012). Continuous PFs can be obtained from a lignin/PAN blend by conventional wet spinning as described by Husman (2012), while CFs with a tensile strength and a tensile modulus of about 2.24 GPa and 217 GPa, respectively, were obtained (Husman 2014). However, when lignin contents are above 20%, unacceptable macro-voids are formed in the CFs, which was also observed by Dong et al. (2015). High molecular weight (MW) PAN for blending lignin is one of the remedies for avoiding macro-void formation via increasing the viscosity of the spinning solution (Thunga et al. 2014). One problem is the homogeneous dissolution of the high MW PAN in the spinning solution. Moreover, the high production cost of such CFs is also a challenge.

Liu et al. (2015) reported a novel gel-spinning technique for preparing lignin/PAN blend PFs with -50°C methanol as a coagulation bath, i.e. the coagulated fibers were stored in a methanol bath at -50°C for over 12 h and then the fibers were drawn with a ratio of 13. The gel-spun PAN/lignin (70/30)-based CFs exhibit a tensile strength of 1.72 GPa and a tensile modulus of 230 GPa, and there are no voids observable in the cross-sections of the fiber (Liu et al. 2015). However, a technical challenge of this approach is the harsh process condition.

In the present study, a wheat straw lignin (WSL) was blended with a commercial textile-grade PAN polymer for PFs. This PAN is cheap and has a good solubility. Continuous PFs were prepared from the blends by a conventional wet spinning process and then converted into PFs via thermal stabilization and carbonization. The PFs were characterized by scanning electron microscopy (SEM), Fourier-transform infrared (FTIR) spectroscopy and differential scanning calorimetry (DSC). The stabilization of the PFs and the structure and composition of the final CFs are addressed.

Materials and methods

A WSL was provided by Anhui Geyi Co., Ltd. (China) and used after purification by desalting with diluted HCl. A commercial textile-grade PAN polymer powder (provided by Zhejiang Hangzhouwan Co., Ltd., China) and dimethyl sulfoxide (DMSO) (from Sinopharm Chemical Reagent Co., Ltd., China) were used as received. Deionized water was produced in our own laboratory.

A series of spinning solutions were prepared by blending different ratios of the WSL and PAN polymer in DMSO (for composition see Table 1). The ratio of PAN/DMSO was fixed to 20/80 by weight, but the WSL content in the blends varied from 0, 5, 15, 20, 30 to 40%; and the solid content of the spinning solution increased correspondingly from 20, 20.8, 22.7, 23.8, 26.3 to 29.4%.

Table 1: Composition of the spinning solutions.

Materials	Lignin content in solution (%)					
	0	5	15	20	30	40
Lignin (g)	0	1	3.53	5	8.6	13.3
PAN (g)	20	20	20	20	20	20
DMSO (g)	80	80	80	80	80	80
Total (%)	20	20.8	22.7	23.8	26.3	29.4

Lignin and PAN were dissolved in DMSO at 60°C for 24 h under continuous agitation, and then deaerated under static condition at 60°C for 12 h. The spinning solution was extruded through a spinneret (50 holes, 0.1 mm diameter) into a water coagulation bath. The total stretch ratios were 3.

The PFs were placed into an air furnace and heated from 200 to 250°C at a heating rate of $1^{\circ}\text{C min}^{-1}$, and the final temperature was maintained for 0.5 h. The thermo-stabilized fibers were carbonized under nitrogen atmosphere by heating from room temperature to 700°C , and the final temperature was maintained for 20 min, and then heated to 1400°C , and maintained at this temperature for 10 min. The heating rate was $10^{\circ}\text{C min}^{-1}$.

The viscosity of the spinning solutions was tested by a DV-II+Pro rotational rheometer of the Brookfield Company (USA) at 60°C at a rotation rate of 5 rpm. The number average molecular weight (M_n) and weight average molecular weight (M_w) data were obtained by gel permeation chromatography (GPC) (TOSOH HLC-8320, Japan) equipped with a refractive index (RI) detector, and then the dispersivity (M_w/M_n) was calculated. The mobile phase was 0.01 mol l^{-1} LiBr/dimethylformamide (DMF) (40°C).

FTIR spectra were recorded on a Thermo Nicolet Nexus 470 FTIR spectrometer using the KBr pellet technique (32 scans at a resolution of 4 cm^{-1}). DSC analysis was carried out on a NETZSCH STA 449 thermal analyzer under air atmosphere at a rate of $10^{\circ}\text{C min}^{-1}$ from room temperature to 500°C . SEM images of the PFs and CFs were produced by a Hitachi S-4800 field-emission scanning electron microscope (FEM), while the samples were sputter-coated with gold before imaging. The average fiber diameter was obtained by measuring 10 fibers randomly on the SEM images.

Results and discussion

PAN exhibits a sharp and narrow GPC profile in shorter retention times, while the lignin GPC profile is broad at longer retention times (Figure 1a). Accordingly, lignin is more polydisperse, which causes the known poor spinnability (Li et al. 2017). On the other hand, PAN has a higher MW and a more uniform MW distribution (MWD) (Table 2). PAN is a linear long-chain polymer and predestined for improving the lignin's spinnability in lignin/PAN blends.

The IR band of PAN (Figure 1b) at 2243 cm^{-1} is assigned to $\text{C}\equiv\text{N}$ stretching vibration in PAN unit. The band at about 1736 cm^{-1} is due to the $\text{C}=\text{O}$ stretching vibration of vinyl acetate (VAc). The bands of the stretching and bending

Figure 1: (a) GPC curves and (b) FTIR spectra of lignin and PAN.

Table 2: Molecular weight and its distribution of PAN and lignin.

	Mn	Mw	Mw/Mn
PAN	7.1×10^4	33.9×10^4	4.8
Lignin	112	7.7×10^4	690.6

vibration of CH₂ are observed at 2939 and 1455 cm⁻¹, respectively. The bands at 1423, 1513 and 1597 cm⁻¹ originate from the lignin's aromatic skeletal vibrations, and the aromatic ring vibration is seen at 1462 cm⁻¹. The appearance of the bands in the range of 1266 to 1330 cm⁻¹ is typical for guaiacyl and syringyl groups in lignin (Boeriu et al. 2004). The band at 1707 cm⁻¹ is due to carbonyl/carboxyl groups.

As is visible in Figure 2a, the viscosity of the spinning solutions first increases gradually with increasing lignin content in the blends, which is highest at 30% lignin content. Interestingly, the viscosity decreases again at lignin concentrations >30%. The viscosity of concentrated polymer

Figure 2: (a) Viscosity of the spinning solutions and (b) the diameter of PFs.

solutions is due to the internal friction of the polymer molecules (Shan et al. 2009), which is caused by the intermolecular forces between them (Doi and Edwards 1978). In the spinning solution in focus, PAN molecules are dispersed in the solution in the form of random coils, which are twisted and form a network structure, while the PAN-PAN intermolecular forces on the knots contribute primarily to viscosity. Below 30% lignin concentration, the increased PAN-lignin intermolecular forces contribute mainly to the increase of the solution's viscosity. However, at higher lignin concentrations, the weak lignin-lignin intermolecular forces begin to dominate, and, as a consequence, the viscosity decreases. The lignin molecules increasingly fill the space between the network of PAN molecules, which will be then more isolated from each other, and thus the strong PAN-PAN intermolecular forces are destroyed. Because of the low MW of lignin, the viscosity of the spinning solution decreases again.

The diameters of the PFs with different lignin contents are presented in Figure 2b. The fiber diameters first

decrease with increasing lignin contents because of the first viscosity increment (Figure 2a). A higher viscous solution extrudes out of the spinneret at a lower rate and this results in smaller fiber diameters. On the other hand, at lignin concentrations $>40\%$, i.e. at lower viscosities, the fiber diameters increase correspondingly.

In the photograph of the PFs in Figure 3a, the pure PAN-PFs are white; while the lignin/PAN blend PFs are brown. The color of the blend gradually deepens with

increasing lignin contents. As is visible on the SEM images in Figure 3b, all the PFs have a noncircular cross-section, which is mainly because of the poor hydrophilicity of the commercial textile-grade PAN polymer. In addition, a pure water coagulation bath was used for fiber spinning resulting in a rapid counter diffusion rate due to the large concentration difference between the spinning solution and the coagulation bath. The fiber epidermis was solidified fast before the solidification of the fiber's interior. As

Figure 3: (a) Photograph and (b) SEM images of PFs, and (c) SEM images of CFs.

as a result, a heterogeneous radial structure was formed, which shrunk unevenly during stretching and drying, leading to noncircular cross-sections. Below 20% lignin concentration, the PFs have a dense structure without any visible macro-voids (Figure 3b). But around 30 and 40% lignin contents, macro-voids appear in the center of the PFs. The morphology of the CFs is inherited from the PFs (Figure 3c), and both of them represent the corresponding morphologies.

The solid content of the spinning solution increased with increasing lignin contents (Table 1). The macro-voids are a manifestation of phase separation between lignin and PAN because of their different hydrophilicity. Lignin contains more hydrophilic OH groups with the tendency to form intermolecular hydrogen bonds, which leads to a single phase between lignin molecules. On the other hand, the intermolecular dipole-dipole interaction among the PAN body also leads to the formation of another single phase due to strong polar nitrile groups. It is also obvious that the high MW PAN form more tight structures than the low MW lignin, which also contributes to phase separation.

Figure 4: (a) FTIR spectra and (b) lignin content of PFs.

Figure 4a shows the FTIR spectra of PFs. The 2243 cm⁻¹ band corresponds to the C≡N group of PAN; the 1513 cm⁻¹ band is for the aromatic ring of lignin. The spectra show that lignin and PAN are a simple mixture without chemical bonds between them. However, with increasing lignin contents, the 2243 cm⁻¹ band (C≡N group of PAN) decreases and the 1513 cm⁻¹ band (aromatic ring of lignin) increases gradually. Thus, the relative lignin content of the PFs can be calculated based on the band ratios A_{1513}/A_{2243} . The corresponding calibration plots are presented in Figure S2 in the Supplementary Material.

The actual lignin content and the lignin yield of the lignin/PAN blend PFs are presented in Figure 4b, which are somewhat lower than the lignin content in the blend spinning solutions. This is because lignin was partially washed out during spinning. When the lignin content in the spinning solutions is between 20 and 30%, the lignin yield in the PF is about 92%. At higher lignin concentrations, the lignin yield decreases to values around 87%.

The DSC curves (Figure 5) of PAN exhibits a strong exothermic maximum, which is attributed to both the cyclization and oxidation reactions (Arbab et al. 2014). The initiation temperature of PAN is around 250°C because of the presence of ester comonomers (VAc), which need higher activation energy for cyclization (Ouyang et al. 2008). The lignin shows a very strong and broad exothermic profile, which is mainly due to the intermolecular crosslinking and repolymerization of the smaller molecules formed via bond cleavage (Oroumei et al. 2015). The initiation temperature of lignin is around 190°C due to its higher thermoreactivity. The maxima of lignin/PAN blend PFs moves to the lower temperature range compared to that of pure PAN PFs. The initiation temperature of the lignin/PAN blend PFs decreased to about 190°C, which is close to that of lignin.

Figure 5: DSC curves of lignin and lignin/PAN blend PFs.

With increasing lignin contents, the exothermic band of the lignin/PAN blend PFs becomes stronger. Probably, the carbonyl/carboxyl groups of lignin are able to initiate the cyclization reaction by ionic mechanism at lower temperatures (Ouyang et al. 2008). As a result, thermal stabilization can be carried out at lower temperatures, which can contribute to lowering the production costs.

Figure 6a shows the density of PFs and thermo-stabilized fibers. The densities of these materials increase with increasing lignin contents because of the higher density of lignin. The density differences between PFs and thermo-stabilized fibers were calculated (see Figure 6a). As is visible, the density differences significantly increased at higher lignin contents.

Figure 6b shows the FTIR spectra of thermo-stabilized fibers. The extent of the cyclization reaction was calculated using the equation $E_c = A_{1595}/A_{2243}$ (Ouyang et al. 2008) and the data are listed in Table 3. As not otherwise expected, E_c values increase significantly with increasing lignin contents.

Because of the large fiber diameter, the mechanical properties of the CFs are not satisfactory. The tensile

Table 3: The extent of cyclization reaction (E_c values) of thermo-stabilized fibers.

	Lignin content in thermo-stabilized fibers		
	20%	30%	40%
E_c value	0.97	1.17	1.56

Figure 7: Element content of CFs.

Figure 6: (a) Density and (b) FTIR spectra of thermo-stabilized fibers.

strength of the CFs is only 300–500 MPa, and the tensile modulus is below 100 GPa. Figure 7 shows the element content of CFs with different lignin contents. According to the elemental composition of lignin and PAN, the oxygen content increases significantly, and the contents of nitrogen and carbon element decrease slightly with increasing lignin contents up to 20%. At higher lignin contents, the elemental composition changes further in the same direction, but the carbon content remains around 95%. It is not exactly clear why the carbon content is so stable.

Conclusions

The viscosity of the spinning solutions and the structure of the PFs were significantly affected by the lignin content in the blends, while the changes are closely related to the intermolecular forces in the spinning solution. Lignin plays a similar role as the carboxylic acid comonomer and results in a significant decrease of the initiation temperature of the exothermic maximum in the DSC profiles. The thermal stabilization of the lignin/PAN blend PFs was significantly promoted by lignin, which contributes to lowering the production cost of CFs. The morphology of the CFs is inherited from the PFs. When the lignin content was increased to

30–40%, macro-voids became visible in the center of the CFs. Thirty percent of the blended lignin content seems to be an insurmountable bottleneck for the preparation of CFs based on lignin/PAN blends. A positive finding is the high carbon content ($\approx 95\%$) of the CFs, and thus lignin could be used for blends, if its concentration is not above 20%.

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