Low cost carbon fibers from bio-renewable Lignin/Poly(lactic acid) (PLA) blends

CrossMark

Shichao Wang, Yan Li, Hengxue Xiang, Zhe Zhou, 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

A B S T R A C T

We report that cylindrically shaped Lignin/PLA based carbon fibers having tensile strength between 258.6 and 159.2 MPa and tensile modulus ranging from 1.7 to 11.6 GPa can be prepared by melt spinning of Lignin/PLA blends followed by the thermal stabilization and carbonization of Lignin/PLA fibers. The introduction of PLA increased the spinnability of Lignin/PLA blends by employing the good spinnability of PLA, to produce continuously spooled Lignin/PLA fibers. The hydrogen-bonding interaction between lignin and PLA phases, demonstrated by DSC and FTIR, increased the tensile modulus of the blend-based carbon fibers relative to that from lignin. However, the tensile strength of Lignin/PLA based carbon fibers was decreased mainly due to the presence of voids that were caused by the volatilization of PLA in the thermal stabilization and carbonization processes.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Carbon fibers are defined as fibers with a carbon content of at least 92% made from polymeric precursors or carbon allotrope building blocks [1]. High tensile strength and modulus, low density, excellent creep and chemical resistance make carbon fibers attractive in aerospace, military and other high technology fields. Currently, carbon fibers are mainly manufactured from petroleum-based poly(acrylonitrile) (PAN) feedstock by solution spinning [2]. With the increasing concerns for the shortage of petroleum resources and the environmental pollution, non-petroleum based precursors combined with environmental friendly spinning methods are preferred for the production of carbon fibers. In addition, the high cost of carbon fibers restricted their further application in general fields, especially in that of light-weight vehicles [3]. Therefore, it is crucial to develop low cost carbon fibers from bio-renewable precursors.

Among bio-renewable materials, lignin is an ideal candidate for the manufacture of carbon fibers due to its high carbon content. As the nature's dominant polymer and the by-product of pulping, lignin is found in most terrestrial plants in the approximate range of 15%–40% dry weight [4,5]. Low cost, bio-renewable and melt processable make it even more attractive. According to the difference of structures, lignin can be grouped into three types: hardwood lignin, softwood lignin and grass lignin. The structure of these three types differs in the monolignols from which the corresponding lignin is built (Fig.S1) [1]. Hardwood lignin is composed of syringyl (S) and guaiacyl (G) units and softwood lignin has predominantly G units, while grass lignin is constructed with S, G and *p*-hydroxyphenyl (H) units. Both hardwood and softwood lignin are used to prepare carbon fibers by melt spinning method [6,7]. However, continuously spooled lignin fibers are hard to obtain without the pretreatment of lignin. The purity of lignin is a critical factor for achieving continuously spooled fibers. Baker et al. [2] extracted the hardwood lignin with organic solvents and obtained fine lignin filaments by melt spinning. The glass transition temperature (Tg) of lignin decreased from 130.2 °C to 88.0 °C after purification, resulting in the adhesion of fibers during the thermal stabilization process. Different from the organic extraction, the purification of lignin using ceramic membrane can also effectively remove the impurities but with just a slight decrease of the Tg of lignin [8]. Nordstrom et al. [9,10] blended kraft lignin with kraft lignin permeate and prepared the lignin based carbon fibers successfully. Unfortunately, the mechanical properties of hardwood lignin based carbon fibers were not mentioned in their study. In addition to purification, chemical modification is also a crucial step. The melt ability of lignin can be improved by acetylation and esterification to

a certain extent, but their cost is relatively high [11,12]. An inexpensive and convenient method to improve the spinnability of lignin is the blending of other polymer. Synthetic polymers were thermally blended with lignin to manufacture lignin based carbon fibers by Kubo et al. [13,14], both poly(ethylene terephthalate) (PET)/lignin and polypropylene (PP)/lignin blends were easily spun into fibers. Additionally, poly(ethylene oxide) (PEO) was also studied to facilitate the lignin spinnability [15,16]. However, developing a precursor utilizing a petroleum-based polymer may pose future problems considering limited oil reserves, which ultimately results in high price volatility for the precursor [17]. In this case, bio-renewable polymers play an irreplaceable role in acting as the plasticizer during the melt spinning process of lignin. Thunga et al. [17] prepared lignin based carbon fibers from a blend of butyrated softwood lignin and PLA, a biopolymer derived from corn, potato and other biomass materials [18,19]. Continuously spooled butyrated lignin (B-Lignin) and B-lignin/PLA fibers were obtained. The spinnability and tensile strength of B-lignin/PLA fibers were both improved with the addition of PLA. However, the post-carbonized fibers with 90 and 100 wt.% of B-lignin deformed from their initially cylindrically shapes to profiles with a flat surface because of the softening of the fibers. Besides, the high content of PLA in B-lignin/PLA blends produced many voids in the fibers after carbonization, making it difficult to determine the mechanical properties of B-lignin/PLA based carbon fibers.

In the present work, the lignin structure before and after purification using ceramic membrane was characterized. Continuously spooled lignin fibers and cylindrically shaped lignin based carbon fibers were manufactured by blending lignin with PLA. The thermal properties of Lignin/PLA blends, the interaction between lignin and PLA phases, the morphology and mechanical properties of lignin and Lignin/PLA blends based carbon fibers were investigated to give a comprehensive approach on the manufacture of low cost carbon fibers from a bio-renewable precursor.

2. Material and methods

2.1. Materials

Hardwood kraft lignin was kindly provided by Suzano Papel e Celulose S.A. Corp., Brazil. The chemical properties of purified lignin are shown in Table S1. PLA with a weight-average molecular weight (M_w) of 1.77×10^5 and a polydispersity index (PDI) of 1.3 was supplied by Nantong Jiuding Biological Engineering Co., Ltd, Jiangsu, China. Deuterated dimethyl sulfoxide (DMSO-d_6) used for ^{13}C NMR analysis was purchased from Sigma—Aldrich. Other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd (China) and were all used as received without further purification.

2.2. Purification of lignin

Lignin was dissolved in sodium hydroxide solution (pH = 12) and fractionated through ceramic membrane with the molecular mass cut-off value of 15 KDa (as given by the manufacturer: Laungy Membrane Filtration Technology, Shanghai, China). Next, sulfuric acid was added to precipitate lignin from the permeate by adjusting the pH of the solution to 2. The precipitated lignin was filtered and washed with deionized water repeatedly to neutralize the pH value. The neutralized lignin was dried at 80 °C for 12 h and heat-treated at 200 °C for 1 h under vacuum to remove moisture and volatiles.

2.3. Preparation of Lignin/PLA fibers

Lignin powders and PLA pellets were mixed together in a Haake Rheocord 90 batch mixer at 220 °C for 5 min with the roller speed of 50 rpm. The contents of PLA were 0, 5, 10, 15 and 20 wt.% of the total weight, respectively. All the Lignin/PLA blends were fed into a twin screw micro-compounder equipped with a take-up device and processed at temperatures of 220 °C—240 °C depending on the content of PLA. The winding rate was 100 m/min and Lignin/PLA fibers were collected on cylinders.

2.4. Thermal stabilization and carbonization of Lignin/PLA fibers

Lignin/PLA fibers were thermally stabilized and carbonized in an oven. The thermal stabilization process was carried out in an air environment. Lignin/PLA fibers were heated from 60 °C to 280 °C at a rate of 0.25 °C/min and held for 1 h before carbonization. The thermally stabilized fibers were subsequently carbonized in a nitrogen atmosphere. The temperature was increased to 1000 °C at a rate of 3 °C/min before cooling to room temperature.

2.5. Structure and properties characterization

Nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker Avance 400 MHz spectrometer at 25 °C in DMSO-d_6.

Differential scanning calorimetry (DSC) analysis was conducted according to the procedure described by Cui et al. [20] using a TA instruments Q20. Samples were heated from 30 °C to 105 °C at a rate of 5 °C/min and then kept isothermally for 40 min prior to being quenched to 30 °C. Next, the DSC thermograms were recorded by increasing the temperature to 250 °C at a rate of 10 °C/min.

Fourier transform infrared spectroscopy (FTIR) was carried out using a Nicolet 8700 Fourier transform infrared spectrometer. All the samples were analyzed using KBr pellet technique and scanned in the range of 4000 to 400 cm^{-1}.

The morphology of Lignin/PLA fibers, before and after carbonization, was characterized using scanning electron microscopy (SEM) (JSM-5600LV, Japan).

The mechanical properties of Lignin/PLA based carbon fibers were measured using a fiber tensile tester (XQ-1A, manufactured by Shanghai Lipu Applied Science Institute). The tensile speed was 5 mm/min with a gauge length of 10 mm. Each fiber diameter result was an average of 5 measurements along the fiber. Tensile strength and modulus values were reported as the average of 10 fibers per sample.

3. Results and discussion

3.1. Chemical structure of lignin before and after purification

The structure of lignin that we used for production of carbon fibers were characterized by a set of multiple nuclei NMR spectra, especially the 2-D HMBC spectrum which reveals the strong coupling between Hs and adjacent Cs among the linkages and the phenyl groups, and was therefore used as the main evidence for the assignment of lignin structure. The ^{13}C NMR spectra of the samples prior to and after filtration through ceramic membrane are shown in Fig. 1(a) and (b), respectively. It can be found that only the signals at 97.3 (artifacts), 65.8—67.1 (C6 in cellulose) and 23.4—33.3 ppm (lipids (CH$_2$) and protein (sc)) were removed after filtration while other resonances remain the same before and after filtration [21—23]. This means that cellulose, carbohydrates and other impurities which are not conducive to melt spinning can be effectively removed by purification. Detailed analysis of the NMR spectra, especially the 2-D HMBC spectrum, reveals that the purified lignin
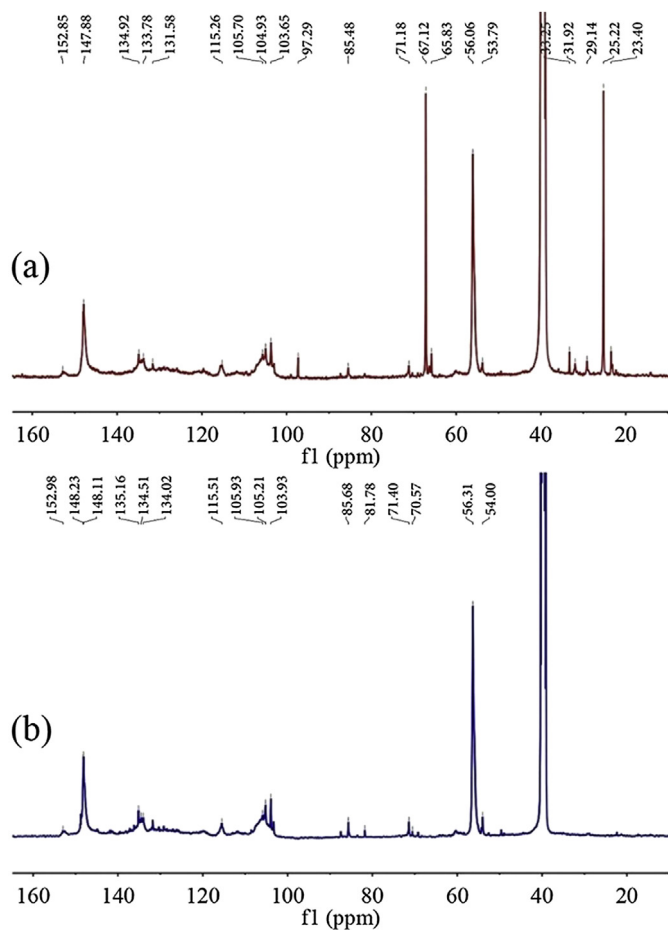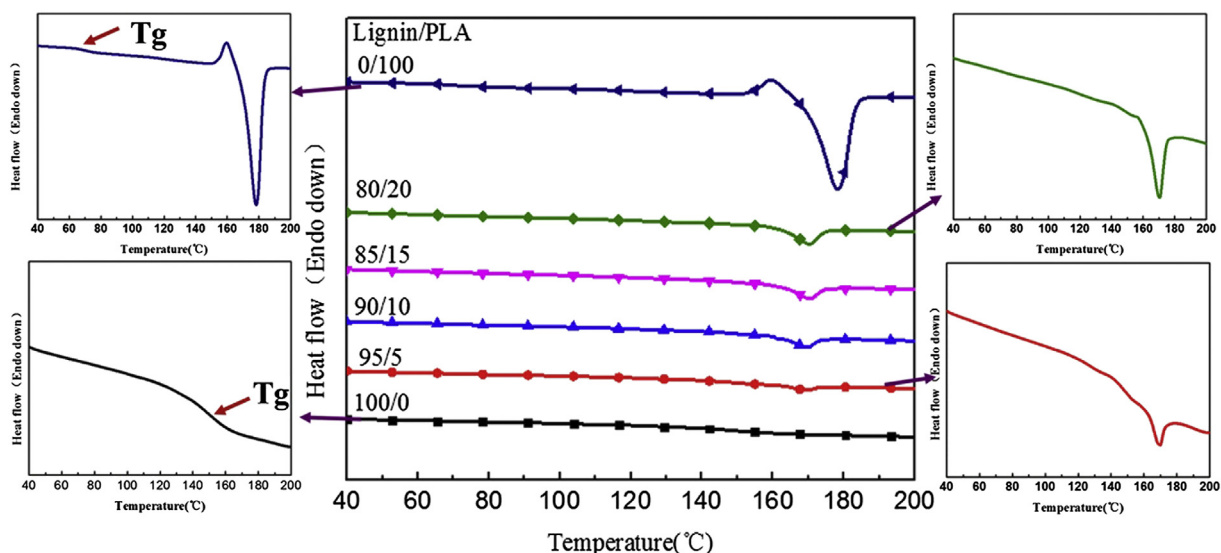
Table 1
Glass transition temperature (Tg), melt temperature (Tm), cold crystallization temperature (Tcc), melt enthalpy ($\triangle H_m$) and cold crystallization enthalpy ($\triangle H_{cc}$) of Lignin/PLA blends.

Lignin/PLA	Tg (°C)	Tm (°C)	$\triangle H_m$ (J/g)	Tcc (°C)	$\triangle H_{cc}$ (J/g)
100/0	149.2	–	–	–	–
95/5	–	169.4	1.8	–	–
90/10	–	169.4	3.9	–	–
85/15	–	170.3	5.5	–	–
80/20	–	170.2	7.2	–	–
0/100	70.1	178.3	45.6	159.8	6.5

3.2. Interaction between lignin and PLA phases

The interaction between lignin and PLA phases in the blends was investigated by DSC. Fig. 2 shows the heating DSC curves of lignin, PLA and the blends with different PLA contents. The corresponding thermal parameters are listed in Table 1. Usually, lignin is considered to have an amorphous structure of aromatic nature with complex connectivity [24,25]. Therefore, no melt peak appeared in the DSC curve of lignin, but a glass transition behavior was clearly observed at 149.2 °C. When PLA was incorporated, the interaction between lignin and PLA phases restricted the motion of lignin and PLA chains, leading to a suppressed glass transition behavior in Lignin/PLA blends and the disappearance of cold crystallization peak of PLA. Besides, the integrity of PLA crystals in Lignin/PLA blends was damaged by the presence of amorphous lignin in comparison with that in neat PLA [26]. As a result, the melting temperature decreased from 178.3 °C of PLA to about 170 °C of Lignin/PLA blends. In addition, the melt enthalpy ($\triangle H_m$) for Lignin/PLA blends increased with the increasing content of PLA due to the crystallized structure of PLA.

To further investigate the interaction between lignin and PLA phases, FTIR was applied to demonstrate the structure difference among lignin, PLA and their blends. As shown in Fig. 3(a), FTIR spectra of lignin and Lignin/PLA blends show a strong O–H stretching absorption around 3494 cm^{-1} and a prominent C–H stretching absorption around 2938 cm^{-1} and 2840 cm^{-1}. The lignin characteristic peaks appeared at 1608 and 1516 cm^{-1}, assigned to the vibration of aromatic skeleton. The appearance of bands around 1322 and 1212 cm^{-1} represents the C–O stretching of S ring and G

Fig. 1. ^{13}C NMR spectra (400 MHz, DMSO-d$_6$) of lignin (a) before and (b) after purification.

contains S and G units together with β-β and β-1 linkages with a linear molecular structure, as shown in Fig. S1–S3. For example, the signal at 81.8 ppm was assigned to the C$_\alpha$ in β-β units, while the peaks at 85.7 ppm and 71.4 ppm corresponded to the C$_\alpha$ and C$_\gamma$ in β-1 units, respectively.
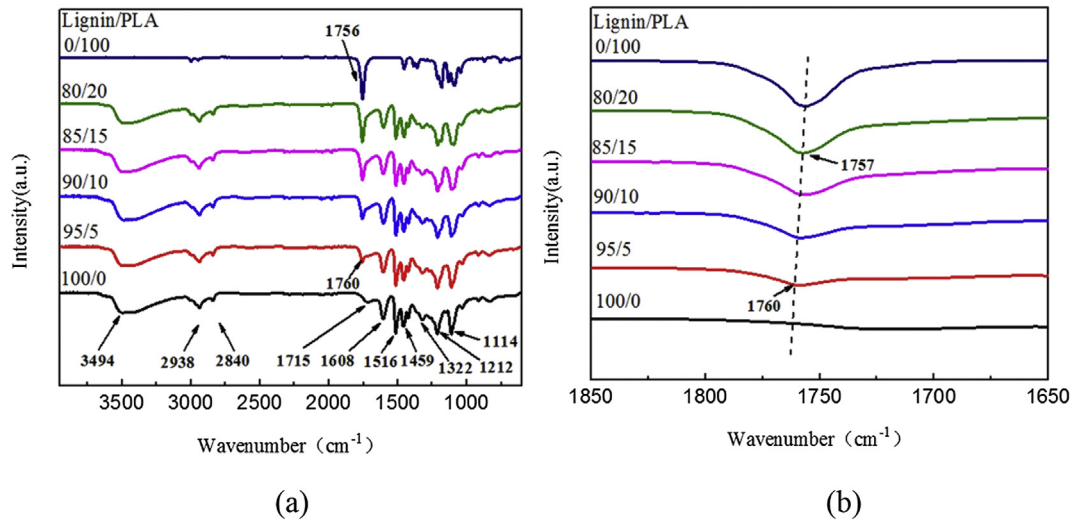

Fig. 2. DSC curves of Lignin/PLA blends.

Fig. 3. (a) FTIR spectra and (b) carbonyl stretching region in the infrared spectra of Lignin/PLA blends.

ring, respectively [27]. The C–H deformation of methyl and methylene and C–H stretching absorption of S and G units appeared at 1459 and 1114 cm^{-1}, respectively. The carbonyl(C=O) stretching band of lignin was reflected at 1715 cm^{-1}, while that of PLA appeared at 1756 cm^{-1}. When 5 wt.% of PLA was added to lignin, the C=O peak of PLA was shifted from 1756 to 1760 cm^{-1} due to the

change in the surrounding environment. Besides, the C=O band of lignin became unobvious compared with that of PLA in Lignin/PLA blends. The amplified spectrum of C=O stretching region is depicted in Fig. 3(b). The C=O band of Lignin/PLA blends was shifted to a lower wavenumber with the increasing content of PLA, from 1760 cm^{-1} of Lignin/PLA 95/5 blend to 1757 cm^{-1} of
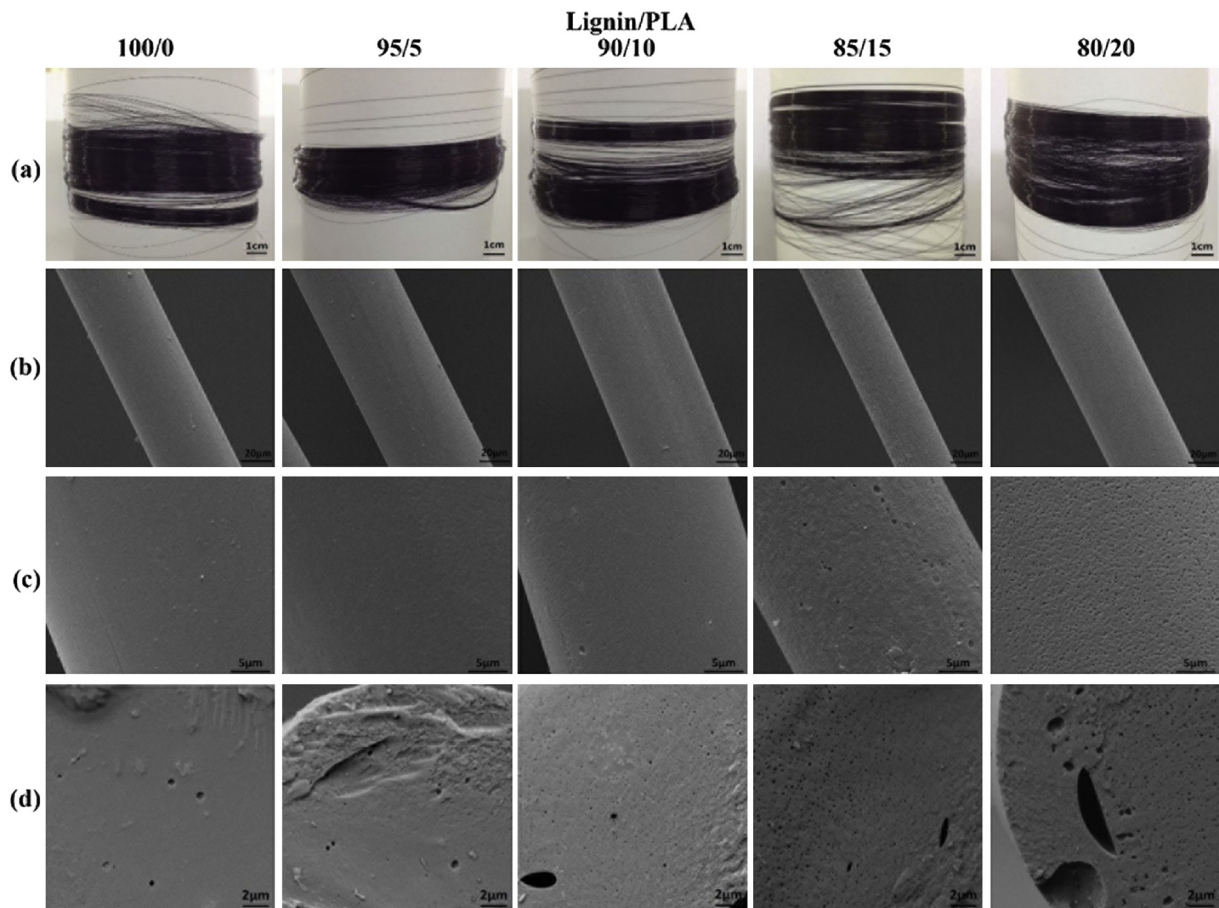

Fig. 4. Continuously spooled fibers and post-carbonized fibers of Lignin/PLA blends. (a. Lignin/PLA fibers spooled on cylinders; SEM images of the overall structures (b) and local amplified images of the surface (c) for Lignin/PLA based carbon fibers; d. Cross-section images of Lignin/PLA based carbon fibers.).
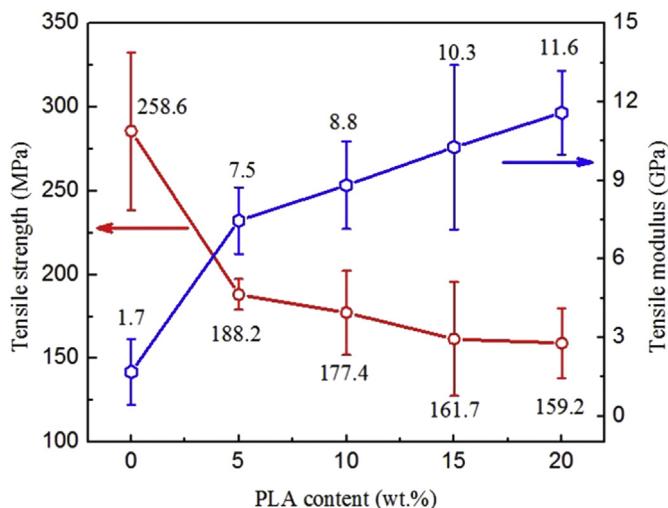
Fig. 5. Tensile strength and tensile modulus as a function of PLA contents for Lignin/PLA based carbon fibers.

Lignin/PLA 80/20 blend. This phenomenon can be attributed to the formation of hydrogen bonds between the −OH groups from lignin chains and the C=O groups from PLA chains. Similar interaction between poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and cellulose nanocrystals (CNCs) has been reported by Yu et al. [28].

3.3. Morphology of Lignin/PLA fibers and their based carbon fibers

Lignin without purification was hard to spin into fibers due to the existence of impurities and lignin-carbohydrate complexes. However, continuously spooled lignin fibers can be easily prepared after purification. Fig. 4(a) depicts the melt processed lignin fiber spools and Lignin/PLA fiber spools. Despite their good spinnability and continuous spinning, the obtained lignin fibers were brittle and present poor mechanical properties. The addition of PLA can improve the toughness of lignin fibers effectively [17], while the thermal stability of Lignin/PLA blends was almost unchanged. Detailed analysis of thermal stability of Lignin/PLA blends and the tensile strength of Lignin/PLA fibers can be found in the Supplementary information.

SEM was utilized to further study the effect of PLA on the morphology of Lignin/PLA based carbon fibers. Fig. 4(b) and (c) show the overall structures and amplified images of Lignin/PLA based carbon fibers, respectively. All of the carbon fibers with the diameter of 30−60 μm exhibited uniform cylindrical structures independently of the composition of the blends. The surface of lignin based carbon fibers was smooth, and some microvoids caused by the volatilization of PLA could be seen on the surface of Lignin/PLA based carbon fibers when 10 wt.% of PLA was incorporated. With the increasing content of PLA, more microvoids appeared on the surface of carbonized fibers. When PLA content was up to 20 wt.%, the surface of Lignin/PLA based carbon fibers became rough and the whole surface was filled up by microvoids. Fig. 4(d) shows the cross-section images of Lignin/PLA based carbon fibers. Due to the presence of a small amount of carbohydrates in lignin, volatile gas was produced during the stabilization and carbonization processes, leading to the formation of some voids in lignin based carbon fibers. Besides, the amount and the size of voids in Lignin/PLA based carbon fibers increased with the increasing content of PLA, due to the coalescence of voids formed by the volatilization of PLA.

3.4. Mechanical properties of Lignin/PLA based carbon fibers

The mechanical properties of Lignin/PLA based carbon fibers were determined by a tensile tester. The tensile strength and tensile modulus for Lignin/PLA based carbon fibers, as a function of PLA content, are shown in Fig. 5. The tensile strength and tensile modulus of lignin based carbon fiber were 285.6 MPa and 1.7 GPa, respectively. Since no tension was applied on the lignin fibers during the thermostabilization and carbonization processes, the mechanical properties were lower than those reported by Kubo et al. [16]. As can be seen in Fig. 5, the incorporation of PLA increased the tensile modulus of lignin based carbon fibers significantly. For instance, the tensile modulus of carbonized fibers increased from 1.7 GPa to 7.5 GPa when 5 wt.% of PLA was added to lignin, and further increased to 11.6 GPa in Lignin/PLA 80/20 blend based carbon fibers. We believe that, as demonstrated in the PET/Lignin analogue [16], the orientation of lignin chains along that of PLA was responsible for the increased tensile modulus of Lignin/PLA based carbon fibers. Normally, the orientation of lignin chains along the axis of fibers was low and the interaction between lignin clusters was very weak, as shown in Fig. 6, leading to a low tensile modulus of lignin based carbon fibers. When PLA was blended with lignin during the melt process, the hydrogen bonds were formed between the chains of PLA and lignin. During the fiber formation process, PLA chains were oriented along the fibers due to its linear structure. The oriented PLA chains dragged the chains of lignin to align along the fibers, leading to an improved orientation of the lignin phase and an increased tensile modulus of carbon fibers.

However, the tensile strength of Lignin/PLA based carbon fibers decreased with the incorporation of PLA. When 5 wt.% of PLA was blended with lignin, although the surface of carbonized fibers were almost not changed, more voids appeared inside the carbonized fibers, leading to a decrease of the tensile strength to 188.2 MPa. When the content of PLA was up to 20 wt.%, and more of continuously interconnected PLA phase has been formed, large voids appeared in the carbonized fibers. These defects caused a large decrease of tensile strength for Lignin/PLA based carbon fibers. We believe that although the orientation of lignin chains can increase the tensile strength of blend-based carbon fibers, the tensile strength of obtained carbon fibers is more dependent on the weak-link effect, such as the voids appeared in the blend-based carbon fibers.
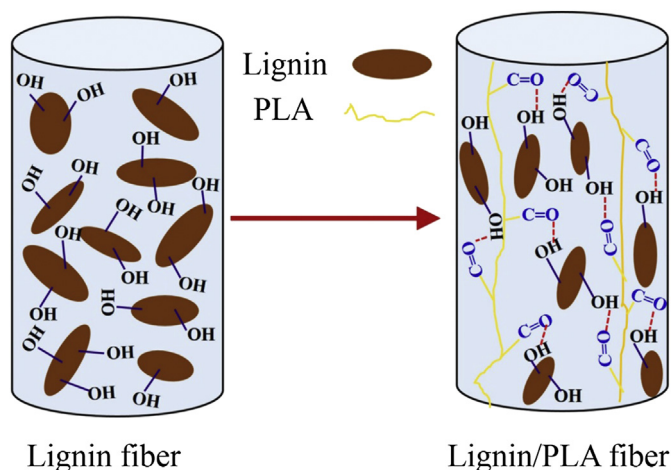

Fig. 6. Schematic diagram of the orientation of lignin and Lignin/PLA fibers.

4. Conclusions

Carbohydrates and other impurities presented in the hardwood lignin have been effectively removed by filtration through ceramic membrane without breaking the basic structure of lignin. Continuously spooled Lignin/PLA fibers and cylindrically shaped Lignin/PLA based carbon fibers were prepared by melt spinning of Lignin/PLA blends followed by the thermal stabilization and carbonization processes of the Lignin/PLA fibers. The introduction of PLA has improved the spinnability of the resultant PLA/Lignin blends compared to that of pure lignin, which would otherwise produce brittle melt spun fibers. The morphology and the mechanical properties of both lignin and Lignin/PLA based carbon fibers were intensively characterized. The volatilization of PLA in the blended fibers during the thermal stabilization and carbonization processes leads to voids on the surface and in the cross-section of fibers, which decreases the tensile strength of Lignin/PLA based carbon fibers. On the other hand, the tensile modulus of Lignin/PLA based carbon fibers, up to 11.6 GPa with a Lignin/PLA ration of 80/20, are much higher than that of pure lignin (1.7 GPa). This increment in tensile modulus was proposed to be caused by the hydrogen-bonding interaction between lignin and PLA phases, which was characterized by FTIR and DSC. Further work is ongoing to improve the mechanical properties of obtained carbon fibers by controlling the porosity formation and optimizing the spinning conditions of Lignin/PLA blends.

Acknowledgments

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.compscitech.2015.09.021.

References

[1] E. Frank, L.M. Steudle, D. Ingildeev, J.M. Spoerl, M.R. Buchmeiser, Carbon fibers: precursor systems, processing, structure, and properties, Angew. Chem. Int. Ed. 53 (21) (2014) 5262–5298.

[2] D.A. Baker, N.C. Gallego, F.S. Baker, On the characterization and spinning of an organic-purified lignin toward the manufacture of low-cost carbon fiber, J. Appl. Polym. Sci. 124 (1) (2012) 227–234.

[3] M.S. Kim, D.H. Lee, C.H. Kim, Y.J. Lee, J.Y. Hwang, C.-M. Yang, et al., Shell-core structured carbon fibers via melt spinning of petroleum- and wood-processing waste blends, Carbon 85 (2015) 194–200.

[4] A.J. Ragauskas, G.T. Beckham, M.J. Biddy, R. Chandra, F. Chen, M.F. Davis, et al., Lignin valorization: improving lignin processing in the biorefinery, Science 344 (6185) (2014) 709.

[5] M.S. Zhou, Z.J. Sun, D.J. Yang, J.H. Huang, X.Q. Qiu, The effect of plasticizer on the properties of alkali lignin/HDPE composites, Acta Polym. Sin. 2 (2014) 210–217.

[6] K. Sudo, K.A. Shimizu, New carbon-fiber from lignin, J. Appl. Polym. Sci. 44 (1) (1992) 127–134.

[7] S. Kubo, Y. Uraki, Y. Sano, Preparation of carbon fibers from softwood lignin by atmospheric acetic acid pulping, Carbon 36 (7–8) (1998) 1119–1124.

[8] I. Brodin, E. Sjoholm, G. Gellerstedt, Kraft lignin as feedstock for chemical products: the effects of membrane filtration, Holzforschung 63 (3) (2009) 290–297.

[9] Y. Nordstrom, I. Norberg, E. Sjoholm, R. Drougge, A new softening agent for melt spinning of softwood kraft lignin, J. Appl. Polym. Sci. 129 (3) (2013) 1274–1279.

[10] Y. Nordström, R. Joffe, E. Sjöholm, Mechanical characterization and application of Weibull statistics to the strength of softwood lignin-based carbon fibers, J. Appl. Polym. Sci. 130 (5) (2013) 3689–3697.

[11] M. Zhang, A.A. Ogale, Carbon fibers derived from acetylated softwood kraft lignin, in: Polymer Precursor-derived Carbon vol. 1173, 2014, pp. 137–152.

[12] W. Thielemans, R.P. Wool, Lignin esters for use in unsaturated thermosets: lignin modification and solubility modeling, Biomacromolecules 6 (4) (2005) 1895–1905.

[13] S. Kubo, J. Kadla, Lignin-based carbon fibers: effect of synthetic polymer blending on fiber properties, J. Polym. Environ. 13 (2) (2005) 97–105.

[14] S. Kubo, T. Yoshida, J.F. Kadla, Surface porosity of lignin/PP blend carbon fibers, J. Wood Chem. Technol. 27 (3–4) (2007) 257–271.

[15] J.F. Kadla, S. Kubo, R.A. Venditti, R.D. Gilbert, A.L. Compere, W. Griffith, Lignin-based carbon fibers for composite fiber applications, Carbon 40 (15) (2002) 2913–2920.

[16] S. Kubo, J.F. Kadla, Kraft lignin/poly(ethylene oxide) blends: effect of lignin structure on miscibility and hydrogen bonding, J. Appl. Polym. Sci. 98 (3) (2005) 1437–1444.

[17] M. Thunga, K. Chen, D. Grewell, M.R. Kessler, Bio-renewable precursor fibers from lignin/polylactide blends for conversion to carbon fibers, Carbon 68 (2014) 159–166.

[18] M. Bulota, T. Budtova, PLA/algae composites: morphology and mechanical properties, Compos. Part A App. Sci. Manuf. 73 (2015) 109–115.

[19] R.L. Yu, L.S. Zhang, Y.H. Feng, R.Y. Zhang, J. Zhu, Improvement in toughness of polylactide by melt blending with bio-based poly(ester)urethane, Chin. J. Polym. Sci. 32 (8) (2014) 1099–1110.

[20] C. Cui, H. Sadeghifar, S. Sen, D.S. Argyropoulos, Toward thermoplastic lignin polymers; part II: thermal & polymer characteristics of kraft lignin & derivatives, Bioresources 8 (1) (2013) 864–886.

[21] J.L. Wen, S.L. Sun, B.L. Xue, R.C. Sun, Recent advances in characterization of lignin polymer by solution-state nuclear magnetic resonance (NMR) methodology, Materials 6 (1) (2013) 359–391.

[22] H. Kono, S. Yunoki, T. Shikano, M. Fujiwara, T. Erata, M. Takai, CP/MAS C-13 NMR study of cellulose and cellulose derivatives. 1. Complete assignment of the CP/MAS C-13 NMR spectrum of the native cellulose, J. Am. Chem. Soc. 124 (25) (2002) 7506–7511.

[23] A. Yamazawa, T. Iikura, A. Shino, Y. Date, J. Kikuchi, Solid-, solution-, and gas-state NMR monitoring of C-13-cellulose degradation in an anaerobic microbial ecosystem, Molecules 18 (8) (2013) 9021–9033.

[24] S. Sen, H. Sadeghifar, D.S. Argyropoulost, Kraft lignin chain extension chemistry via propargylation, oxidative coupling, and claisen rearrangement, Biomacromolecules 14 (10) (2013) 3399–3408.

[25] E. Marklund, J. Eitzenberger, J. Varna, Nonlinear viscoelastic viscoplastic material model including stiffness degradation for hemp/lignin composites, Compos. Sci. Technol. 68 (9) (2008) 2156–2162.

[26] S. Wang, H. Xiang, R. Wang, C. Peng, Z. Zhou, M. Zhu, Morphology and properties of renewable poly(3-hydroxybutyrate-co-3-hydroxyvalerate) blends with thermoplastic polyurethane, Polym. Eng. Sci. 54 (5) (2014) 1113–1119.

[27] K.K. Pandey, A study of chemical structure of soft and hardwood and wood polymers by FTIR spectroscopy, J. Appl. Polym. Sci. 71 (12) (1999) 1969–1975.

[28] H.Y. Yu, Z.Y. Qin, L. Liu, X.G. Yang, Y. Zhou, J.M. Yao, Comparison of the reinforcing effects for cellulose nanocrystals obtained by sulfuric and hydrochloric acid hydrolysis on the mechanical and thermal properties of bacterial polyester, Compos. Sci. Technol. 87 (2013) 22–28.