

Carbon Fibers Derived from Pure Alkali Lignin Fibers Through Electrospinning with Carbonization

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Alkali lignin (AL) fibers with a smooth surface and fine morphological appearance were successfully produced *via* electrospinning using a simple heated single spinneret system, instead of typical electrospinning of lignin with added synthetic polymer blends or conventional co-axial electrospinning. To reduce the size of the fibers, glycerol was added to the spinning solution as a co-solvent for surface tension reduction and electrospinnability improvement. After electrospinning, stabilization and carbonization were subsequently performed to convert AL fibers to carbon fibers (CFs). The obtained CFs displayed rough and uneven surfaces. However, the CFs derived from glycerol-added solution showed greater electrical conductivity, specific surface area, and porosity compared with those from pure AL solution. Furthermore, the results indicated that the inorganic salts on the rough surface of CFs were successfully removed by sulfuric acid (H₂SO₄) washing. After H₂SO₄ washing, the CFs revealed a smoother surface and higher electrical conductivity, specific surface area, and porosity.

Keywords: Carbon fibers; Alkali lignin; Electrospinning; Carbonization; Electrical conductivity

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INTRODUCTION

Carbon fibers (CFs) are carbon materials that contain more than 95% carbon and have a lamellar graphite-like structure, possessing unique properties (*i.e.*, chemical, mechanical, and electrical) including light weight, high tensile modulus and strength, and high thermal or electrical conductivity (Svinterikos and Zuburtikudis 2016). These properties enable them to be widely used in many fields of applications, such as automotive and aerospace industries (Dai *et al.* 2018), and composites (Matsuo 2008).

The global requirement of CFs has particularly increased, of which most of the requirement is in the automotive and aerospace industries (Jacob 2014). Their excellent lightweight character helps improve fuel efficiency and offset battery weight (Adam 1997; Jacob 2014). Moreover, advanced technologies have recently improved various properties of CFs by reducing their diameter, and resulting CFs also have been utilized in other interesting applications, such as filtration technology (Thiruvengkatachari *et al.* 2009), catalysis (Yang *et al.* 2015), and electrochemical energy storages (Javaid 2017).

Currently, commercial CFs have been produced from petroleum-based resources (*i.e.*, polyacrylonitrile (PAN) or pitch) as main precursors that are relatively expensive and

not environmentally friendly. However, their high cost and limited supply of precursors are important problems of CFs for practical applications (Baker and Rials 2013; Wang *et al.* 2013). Therefore, many researchers are searching for alternative precursor materials that are low-cost and environmentally friendly to produce CFs with acceptable properties compared with the petroleum-based ones (Sen *et al.* 2015; Berenguer *et al.* 2016).

Among renewable biomass-based precursors, lignin has been actively considered as a low cost precursor for CFs production, because it is a natural biomass source with aromatic properties (Kai *et al.* 2015). The chemical structure of lignin is complex, containing random networks of phenylpropane groups that are composed of carbon, hydrogen, and oxygen. Its monomeric units are *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol (Duval and Lawoko 2014). The ratio of each monomeric unit depends mainly on the different species of plant (Lora and Glasser 2002; Duval and Lawoko 2014). It is a major by-product that is produced in a large quantity annually in the paper pulping and cellulosic-ethanol industries (Jin *et al.* 2014). Despite the wide availability of lignin, there is no large-scale industrial utilization for lignin as any special product. Nevertheless, the great availability of lignin enables it to be considered as an interesting precursor for CFs production (Frank *et al.* 2014).

One of the various methods that have been utilized to produce ultrafine CFs is electrospinning. It has been demonstrated that continuous CFs with controllable diameters can be successfully fabricated. Some electrospun fibers have been converted into CFs (Zhang and Hsieh 2009; Inagaki *et al.* 2012; Schreiber *et al.* 2014). In comparison, lignin fiber productions through electrospinning are relatively challenging because lignin solution has unique molecular entanglement, viscosity, surface tension, and rheological behaviors, which are different from typical electrospinnable polymers. Therefore, several reports demonstrated successful electrospinning of lignin with polymer blends (*i.e.*, polyacrylonitrile (PAN) (Ma *et al.* 2015), polyethylene oxide (PEO) (Dallmeyer *et al.* 2014; Poursorkhabi *et al.* 2015), and polyvinyl alcohol (PVA) (Ago *et al.* 2012)) to improve its electrospinnability.

In the last decade, Ruiz-Rosas *et al.* (2010) successfully produced fibers from pure organosolv lignin (produced from organosolv process, a pulping technique that uses an organic solvent to solubilize lignin and hemicellulose) *via* co-axial electrospinning, where there was a sheath layer of solvent in the co-axial spinneret. The organosolv process has been well known in the pulping industry and has a more environmental friendly character than other lignin production processes. However, the limitation of the organosolv process is low capability to apply for the large-scale industry due to economic non-favorability against the competition of their pulping procedure (Chen 2014). On the contrary, the alkali process is one of the predominant global processes and widely accessible at the industrial scale. Therefore, the alkali lignin (AL) (also known as kraft lignin) is the dominant raw material for various studies, readily available and is considerably cheaper than organosolv lignin (Norberg *et al.* 2013).

Fabrication of ultrafine CFs from AL by electrospinning with some applications have been reported. Hu and Hsieh (2013) reported fabrications of sub-micron activated CFs with high specific surface area by carbonization and activation of electrospun fibers from AL solution blended with PEO. Song *et al.* (2019) stated that activated CFs could be fabricated by electrospinning of AL/PVA blended solution followed by thermal treatment and activation. The CFs obtained showed a great potential application for absorption of volatile organic compounds (VOCs). From the open literature, there is no previous report on the fabrication of ultrafine CFs derived from pure AL using electrospinning with the

single-spinneret system. For this reason, this work was performed with the aim to produce CFs from AL without any added synthetic polymer *via* electrospinning using the single spinneret system with a simple-designed heat method followed by stabilization and carbonization process. The effects of AL solution on the electrospinning performance were explored. After carbonization, the morphology and physical properties of CFs obtained were investigated. Removal of inorganic contaminants from CFs was additionally studied.

EXPERIMENTAL

Materials

Preparation of lignin solutions

Solutions of AL (Catalog number 471003 (water soluble); Sigma-Aldrich, St. Louis, USA) in deionized (DI) water were prepared with various ratios of lignin to water in the range of 1:1 to 1:2 (w/w) under constant stirring. To increase the electrospinnability of the solutions, glycerol (Chemipan Corporation Co., Ltd., Bangkok, Thailand) was used as a co-solvent. The ratios of glycerol to DI water of 0.5:1 to 1:1 (v/v) were studied.

Methods

Electrospinning

The prepared solution was added *via* a 5-mL plastic syringe with the 45°-tilted setup from a vertical orientation (Fig. 1). A blunt-end 20 G needle was used for the single spinneret connected to the positive electrode of a high voltage supply. A plastic plate covered with aluminum foil was used as the collector and connected to the ground. An aluminum pipe (wrapped with insulation tape to protect any electrical charge) with inlet and outlet holes (for 80 °C-hot water flows by using a water pump) was used as a heat jacket for electrospinning. The heat jacket was used to cover the plastic syringe to heat the solution during electrospinning (to enhance electrospinnability of the lignin solution). The solution was electrospun under a fixed applied potential of 20 kV at the collection distance of 15 cm. After electrospinning, the electrospun fibers were then air dried.

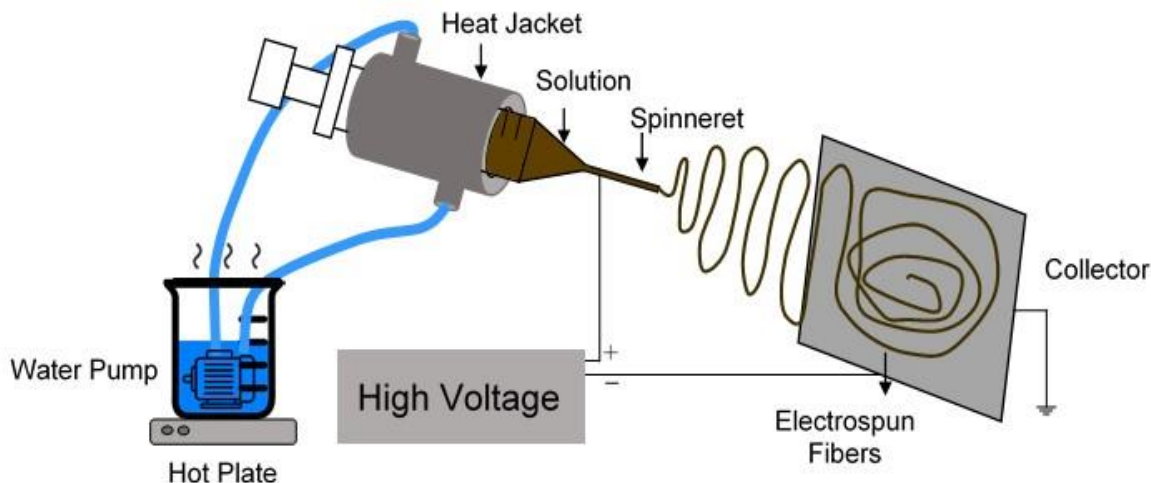


Fig. 1. Schematic illustration of electrospinning procedure of lignin solution with a developed heat jacket

Thermostabilization and carbonization

Thermostabilization of the electrospun fibers was completed at 260 °C for 1 h with a heating rate of 1 °C/min. After thermostabilization, the obtained fibers were carbonized under N₂ atmosphere at 800 °C for 1 h with a heating rate of 5 °C/min.

Characterizations

Fiber morphology was investigated using a scanning electron microscope (SEM, JSM-6610LV; JEOL Ltd., Tokyo, Japan). Electron beam energy of 20 kV was used for analysis. The electrospun fibers and stabilized fibers were coated with a gold (Au) layer using a sputter coater (Cressington 108auto; Cressington Scientific Instruments, Watford, UK) before their SEM examination, whereas CFs were imaged without any Au coating. The viscosities of AL solutions were measured with a viscosity meter (Visco Star Plus (type: Visco Star+ L); Fungilab S. A., Barcelona, Spain). The electrical conductivity of CFs was measured at room temperature using a four-point sheet resistivity meter (Four-point Meter; Yokogawa, Bangkok, Thailand). The elemental composition of CFs was investigated through energy dispersive x-ray spectroscopy (EDS, INCA X-act; Oxford Instruments, Abingdon, UK) and an elemental analyzer (CHNS/O, LECO 628; LECO Corporation, St. Joseph, MI, USA). The basic chemical characteristics were investigated using a Fourier transform infrared spectrometer (FTIR, Perkin Elmer Spectrum One; PerkinElmer Inc., Waltham, MA, USA). Specific surface area (Brunauer–Emmett–Teller (BET) method) and pore characteristics were examined by N₂ adsorption-desorption at 77 K (3Flex Surface Characterization; Micromeritics Instrument Corporation, Norcross, USA).

RESULTS AND DISCUSSION

Electrospun Fibers

In order to produce lignin fibers without adding any synthetic polymer under various conditions, it was found that only droplets were observed from most AL solutions in water. This was attributed to low entanglement of lignin molecules because of high viscosity (Dallmeyer *et al.* 2010). This may be the main reason why there are no reports on electrospinning of purely AL in the literature. Fortunately, at the 1:1.5 w/w ratio of lignin to water, smooth fibers without any beads or droplets with an average fiber diameter of $31.54 \pm 15 \mu\text{m}$ (Fig. 2a) could be electrospun from the heated solution. Chuangchote *et al.* (2009) reported that the high surface tension of water (72.2 mN/m) leads to a large diameter of electrospun fibers from aqueous solution. To reduce the diameter of AL fibers, the mixing of water with a co-solvent that has lower surface tension is an easy way to reduce the surface tension of the spinning solution. It has been reported that the surface tension of sodium alginate (SA) aqueous solution could be decreased and electrospinnability could be improved with the addition of glycerol (Nie *et al.* 2008). Therefore, in this work, glycerol, a low-cost bioreagent with lower surface tension (63.4 mN/m), was used as a co-solvent. Figure 2b shows that finer fibers with an average fiber diameter of $26.11 \pm 8 \mu\text{m}$ could be produced at the ratio of glycerol to water of 0.5:1 v/v (lignin: solvent = 1:1.25 w/w). With increasing the ratio of glycerol to water to 0.75:1 and 1:1, fused beaded fibers were obtained (Figs. 2c and 2d). These results were in line with the physical properties of AL solutions (Table 1). It can be seen that increasing glycerol content led to a significant

decrease in conductivity and an increase in viscosity of the spinning solution (Nie *et al.* 2008).

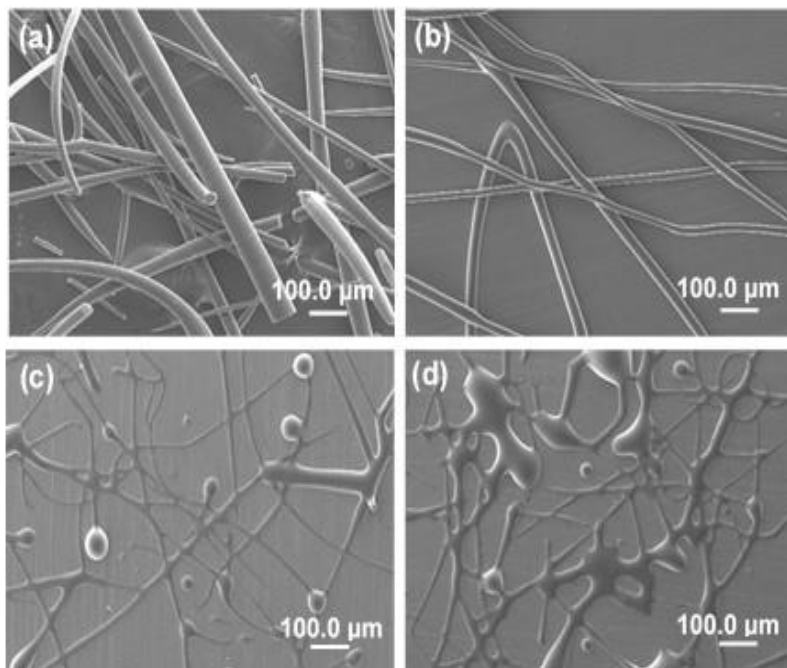


Fig. 2. SEM images of electrospun fibers produced from AL solutions: (a) in water (lignin:water = 1:1.5 w/w); and (b) through (d) in mixed glycerol/water solvent (lignin:solvent = 1:1.25 w/w); the ratios of glycerol to water in the mixed solvent were (b) 0.5:1; (c) 0.75:1; and (d) 1:1 v/v

Table 1. Physical Properties of AL Solutions

Glycerol:Water (v/v)	AL:Solvent (w/w)	Conductivity ($\mu\text{S}/\text{cm}$)	Viscosity (Pa·s)
0:1	1:1.5	1086.29 ± 97.66	93.30 ± 11.13
0.5:1	1:1.25	532.31 ± 42.13	n/a
0.75:1	1:1.25	463.38 ± 28.16	n/a
1:1	1:1.25	385.83 ± 19.51	1204.23 ± 43.32

Stabilized Fibers and CFs

Figure 3 shows micrographs using visible light (for colors of CFs) and SEM images with histograms of the diameters of fibers obtained from electrospinning of AL solutions. The stabilized fibers showed considerably smaller fiber diameters compared with the lignin ones. A smooth fiber surface could be obtained from the stabilized fibers from the AL solution (Fig. 3a2), whereas the stabilized fibers from the glycerol-blended solution showed irregular morphological appearance because of the evaporation of glycerol (Fig. 3b2). The average fiber diameters (thickness) of CFs derived from solutions without and with glycerol co-solvent were $24.55 \pm 9 \mu\text{m}$ (0.098 mm) and $21.05 \pm 9 \mu\text{m}$ (0.084 mm), respectively. CFs obtained from both solutions were black in color, as shown in inset images in Figs. 3a and 3b. The surface of fibers became rough and uneven after the

carbonization (Figs. 3a3 and 3b3). This irregular fiber surface may be attributed to the presence of contaminants caused by invisible inorganics (Song *et al.* 2019). The tensile strengths of commercial PAN-based carbon fiber are in the range of 3 GPa to 7 GPa, while the tensile strength of typical lignin-based CF was only 0.48 GPa (Lin *et al.* 2013). Despite the lower strength properties, lignin-based CFs have substantial potentials for the next generation of alternative electronic and electrode applications (Ma *et al.* 2016; Jayawickramage *et al.* 2019). Therefore, in this work, electrical property was the only focus. Electrical conductivities of CFs derived from lignin solutions without and with glycerol were 2.64 ± 0.68 mS/cm and 5.38 ± 0.18 mS/cm, respectively. This result corresponds to the reported study that the conductivity of fibers increases with reducing fiber diameters (Zhao *et al.* 2018).

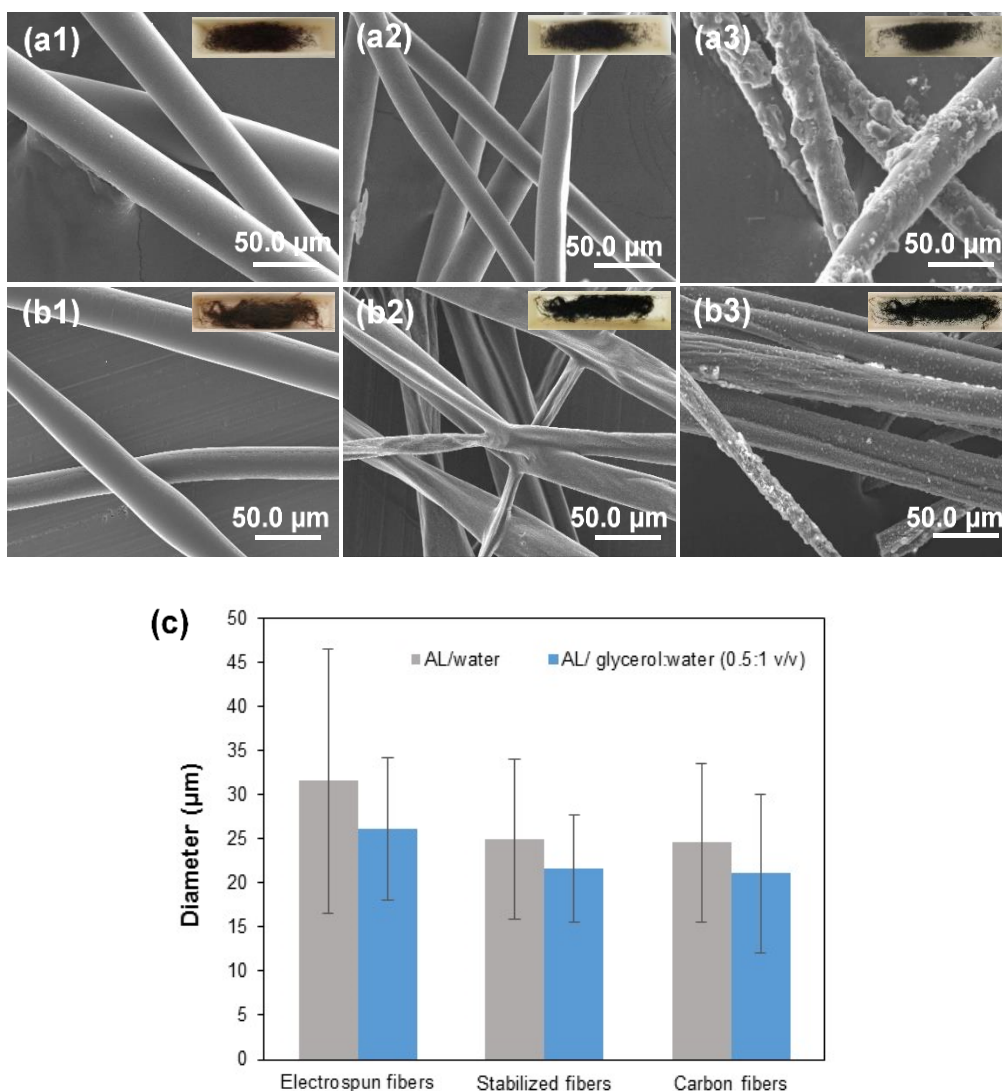


Fig. 3. SEM images of fibers from AL solutions: (a) in water (lignin:water = 1:1.5 w/w); (b) in mixed glycerol/water solvent (lignin:solvent = 1:1.25 w/w, glycerol:water = 0.5:1 v/v) (numbers 1 through 3 refer to electrospun fibers, stabilized fibers, and carbon fibers, respectively); and (c) histograms of the fiber diameters obtained (insets in (a) and (b) are photographic images of fibers in ceramic crucible boats)

Removal of Inorganic Contaminants from CFs

Use of unpurified AL as a precursor for CF fabrications resulted in rough surfaces of CFs obtained due to the presence of inorganic contaminants. From the elemental composition investigation by EDS (Fig. S1), sodium (Na) and sulfur (S) were found as the major impurities in CFs. It should be noted that salts can be present in AL as a result of chemical processes that employ solvents and chemicals (*e.g.* NaOH and Na₂S) during the the production (Srisasiwimon *et al.* 2018). The salt was still in the spinning solution during the electrospinning and remained in electrospun fibers after the solvent evaporation. When the electrospun fibers were heated through the thermal treatment processes (*i.e.* thermostabilization and carbonization) at low temperatures, the inorganic salts solidified and recrystallized on the fiber surface of the CFs obtained (Poursorkhabi *et al.* 2016). A previous study reported that Na content in AL could be reduced by acid washing (Hu and Hsieh 2013). Therefore, in this work, inorganic salts on the surface of CFs were removed by sulfuric acid (H₂SO₄) washing by the following procedure. The CFs were stirred continuously in 5 wt% H₂SO₄ aqueous solution for 4 h. Water rinsing was then completed *via* stirring for 3 h (two times). After that, the CFs were oven-dried overnight. The SEM images of CFs before and after H₂SO₄ washing are shown in Fig. 4. The CFs after H₂SO₄ washing showed a smooth surface without contaminants (Figs. 4a2 and 4b2).

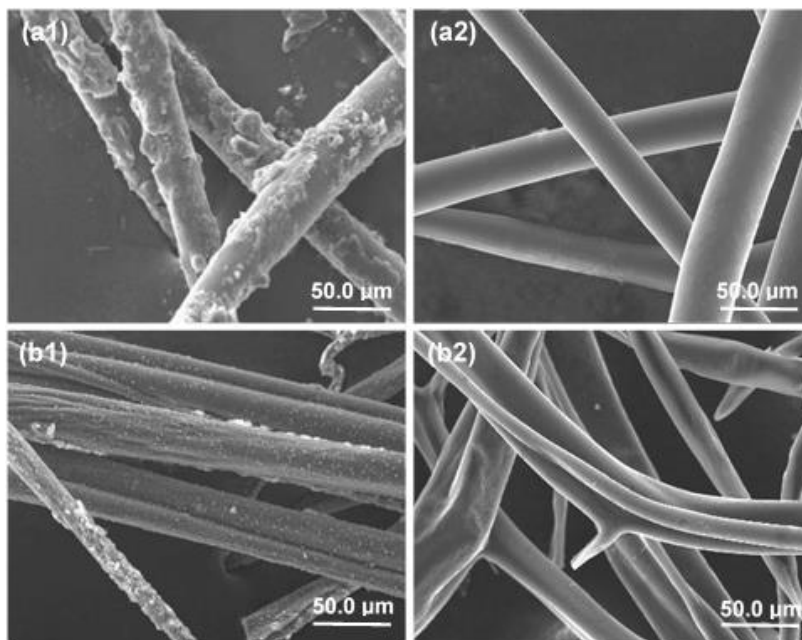


Fig. 4. SEM images of CFs from AL solutions: (a) in water (lignin:water = 1:1.5 w/w); and (b) in mixed glycerol/water solvent (lignin:solvent = 1:1.25 w/w, glycerol:water = 0.5:1 v/v); numbers “1” and “2” refer to before and after H₂SO₄ washing, respectively

Interestingly, the electrical conductivities of CFs after H₂SO₄ washing from the solutions without and with glycerol were 3.09 ± 0.79 mS/cm and 6.07 ± 0.16 mS/cm, respectively, which were remarkably higher than the as-carbonized fibers (17.0% and 12.8% increments, respectively). Alarifi *et al.* (2015) stated that the electrical conductivities of PAN-derived CFs could also be improved after treatment by acids, which has potential to be utilized in strain sensor applications. From the viewpoint of conductivity, focusing on the change of conductivity after acid treatment, lignin-based

carbon fibers may be applied in the sensing applications, *e.g.* chemical sensors. After treatment, the lignin-based carbon fibers have significant potentials for various applications, such as green electrode materials for electronic devices, printable cells, and energy storage applications.

The elemental compositional analysis by elemental analyzer (Table 2) revealed that after H₂SO₄ washing, the carbon contents of CFs from solution without and with glycerol increased from 61.43% to 80.99% and 59.47% to 81.01%, respectively.

Table 2. Elemental Analysis (C, H, N, and S) of CFs under Various Conditions of Raw Solutions before and after H₂SO₄ Washing

Raw Solution for CFs		H ₂ SO ₄ Washing	Elemental Analysis of CFs (%)			
Lignin:Solvent (v/v)	Solvent (Glycerol:Water) (v/v)		N	C	H	S
1:1.5	0:1	Before	0.23	59.47	1.46	3.18
1:1.5	0:1	After	0.28	81.01	1.75	2.12
1:1.25	0.5:1	Before	0.21	61.43	1.19	3.21
1:1.25	0.5:1	After	0.26	80.99	1.62	2.32

Note: Commercial AL powder consisted of 0.14% N, 46.55% C, 4.82% H, and 4.0% S

Chemical structures and functional groups of AL precursor and CFs were investigated by FTIR (Fig. 5). In all spectra, broad absorbance peaks in the range of 3390 to 3220 cm⁻¹ indicating O-H stretching vibration of hydroxyl groups (Zhao *et al.* 2016) and absorbed molecular water on fiber surfaces were observed. In the only-AL precursor spectrum, the O-H stretching peak was extended to the range of 3460 to 3220 cm⁻¹, which was attributed to aliphatic and phenolic hydroxyl groups in the structure of lignin. Moreover, for AL precursor, the following were observed: bands in the range of 2930 to 2833 cm⁻¹ (corresponding to the vibration of C-H stretching of methyl and methylene groups) (El Mansouri *et al.* 2011); the vibrations of C-C bonds and aliphatic C-H, C-O, and C-O-C groups at 1500 to 1000 cm⁻¹; aromatic skeletal vibrations at 1578, 1505, 1464 and 1420 cm⁻¹ (indicating an aromatic functionality of lignin); and peaks in the 900 to 700 cm⁻¹ range (indicating C-H deformation in benzene ring) (Srisasiwimon *et al.* 2018). Considering FTIR spectra of CFs compared with AL precursor, new bands appeared at 2360 cm⁻¹ for CFs, arising from the adsorption of environmental CO₂ (Ray *et al.* 2004). Meanwhile, the four spectra of CFs showed disappearances of aromatic skeletal vibrations, O-H stretching, C-H stretching, C-H deformation (1384 cm⁻¹), and C-O stretching (1263 cm⁻¹). This result corresponds to the decomposition of the majority of lignin side chains after burning at a temperature over 500 °C (Cao *et al.* 2013; Zhang *et al.* 2017; Zhao *et al.* 2018). Carbonization can reduce O-H, C-H, C-O, and phenyl groups, induce closer structures of benzene rings, create cross-links, and finally change the structure to be the network of carbon-six rings (Lin *et al.* 1995; Edie 1998).

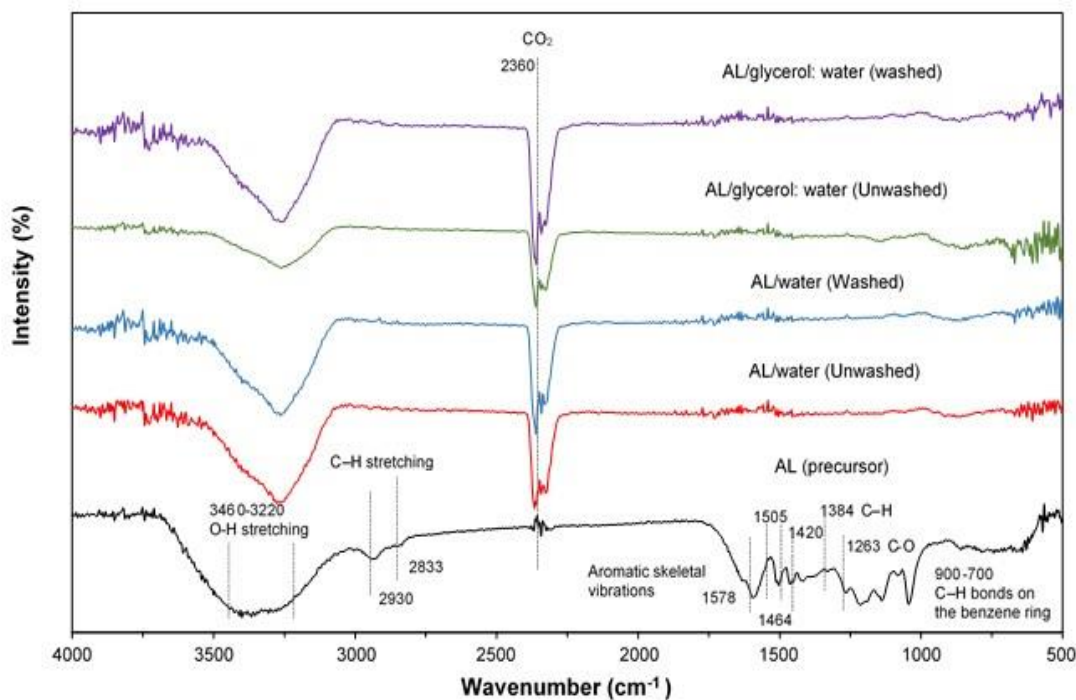


Fig. 5. FTIR spectra of AL precursor and CFs before and after H₂SO₄ washing from AL solutions in water (lignin:water = 1:1.5 w/w) and in mixed glycerol/water solvent (lignin:solvent = 1:1.25 w/w, glycerol:water = 0.5:1 v/v)

Specific Surface Area and Pore Characterizations of CFs

N₂ adsorption isotherms of CFs were used for determination of surface area (Brunauer-Emmett-Teller (BET) method), and N₂ desorption was used for the estimation of pore size and pore volume (Barrett-Joyner-Halenda (BJH) method) of CFs before and after H₂SO₄ washing. Type-IV adsorption-desorption isotherms were found from all samples (Fig. S2), revealing mesoporous structure (meaning that pore sizes are in the range of 2 to 50 nm) with strong adsorbent interactions (Sing 1985; Chen *et al.* 2014). The pore characteristics of CFs testes are listed in Table 3. It was found that CFs derived from AL solutions without glycerol before H₂SO₄ washing had the lowest specific surface area (33.89 m²/g), the largest pore size (4.19 nm), and the smallest pore volume (0.035 cm³/g). This result might be caused by obstruction of gas adsorption and desorption by inorganic salt crystals contained on the rough surface of fibers. After H₂SO₄ washing, BET specific surface area and pore volume of CFs derived from both AL solutions (with and without glycerol) were found to significantly increase, while pore size was found to decrease. The highest specific surface area of 85.67 m²/g and pore volume of 0.072 cm³/g were achieved from CFs derived from AL solutions with glycerol after H₂SO₄ washing (while the specific surface area and pore volume of CFs derived from AL solutions without glycerol after H₂SO₄ washing were 83.41 m²/g and 0.062 cm³/g, respectively, corresponding to the thinner fiber diameters) (Jayawickramage *et al.* 2019). Even though the specific surface areas of CFs derived from AL in this work were lower than PAN-based CFs (700 to 1,200 m²/g) (Inagaki *et al.* 2012) and cellulose/polymer-derived-activated CFs (870-1,400 m²/g) (Ogale *et al.* 2016), the surface areas of AL-derived CFs were still higher than the CF mats derived from organosolv lignin (8-37 m²/g) (Tenhaeff *et al.* 2014). CFs derived from AL

in this work are still promising as a starting point for future studies in many advanced applications such as electrochemical energy storage and electrode applications.

Table 3. Surface Area and Pore Characteristics of CFs Fabricated from Various Conditions of Raw Solutions before and after H₂SO₄ Washing

Raw Solution for CFs		H ₂ SO ₄ Washing	BET Surface Area (m ² g ⁻¹)	Pore Size (nm)	Pore Volume (cm ³ g ⁻¹)
Lignin:Solvent (v/v)	Solvent (Glycerol:Water) (v/v)				
1:1.5	0:1	Before	33.89	4.19	0.035
1:1.5	0:1	After	83.41	3.43	0.062
1:1.25	0.5:1	Before	65.99	3.75	0.060
1:1.25	0.5:1	After	85.67	2.97	0.072

CONCLUSIONS

1. Electrospun fibers with smooth surfaces and fine morphologies from pure AL solutions were successfully produced by electrospinning using a simple heated single spinneret system.
2. With mixing of small amount of glycerol as a co-solvent in AL solutions, smooth fibers with smaller diameters were achieved due to decreased surface tension of the spinning solution and improved electrospinnability.
3. The fibers obtained were successfully converted into CFs with a rough and uneven surface *via* thermal processes. The CFs derived from glycerol-added solution showed greater electrical conductivity, specific surface area, and porosity compared with those from the pure AL solution.
4. Inorganic salts on the surface of CFs were successfully removed *via* H₂SO₄ washing. The electrical conductivity, specific surface area, and porosity of CFs after H₂SO₄ washing was obviously improved.
5. This study provides a new solution to solve the problem of electrospinning of pure AL and demonstrated an approach to produce low-cost CFs from a promising bio-based precursor. The derived CFs are promising for the further uses in electronic devices and electrode applications.

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APPENDIX

Supplementary Information

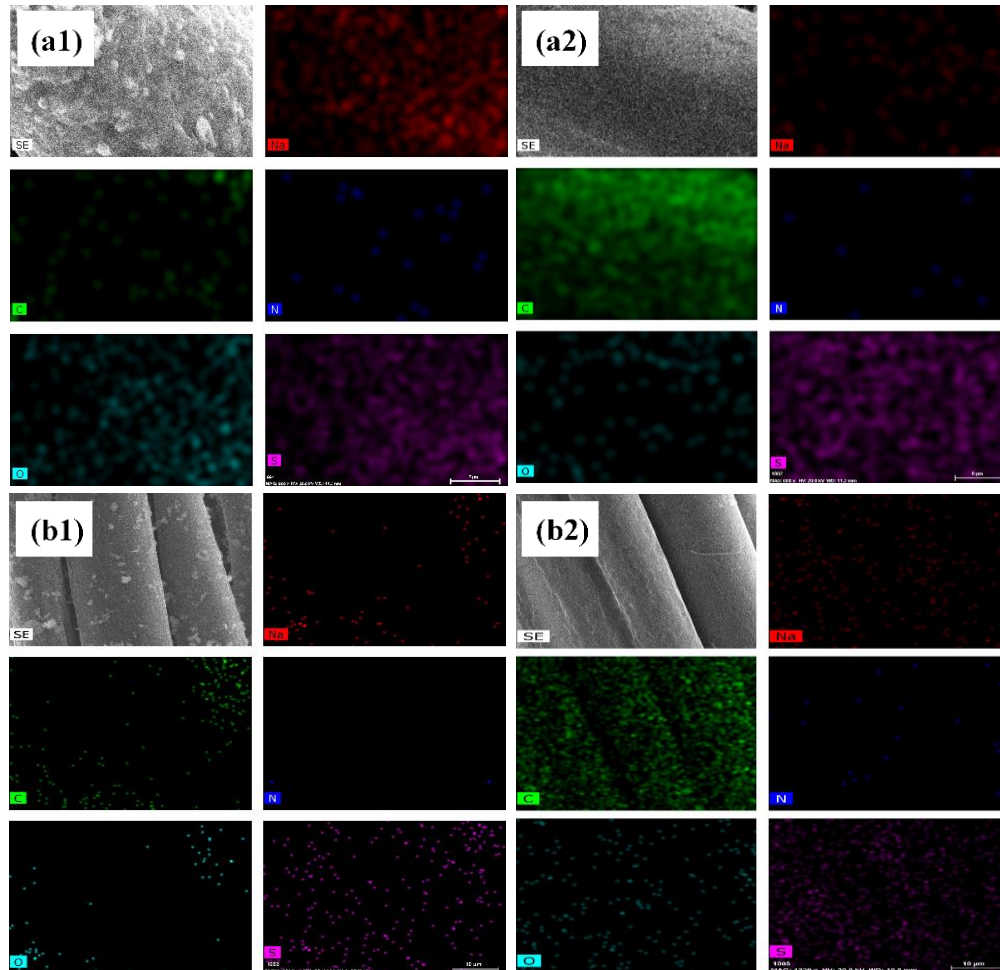


Fig. S1. EDS element mapping of CFs from AL solutions: (a) in water (lignin:water = 1:1.5 w/w) and (b) in mixed glycerol/water solvent (lignin:solvent = 1:1.25 w/w, glycerol:water = 0.5:1 v/v); numbers “1” and “2” refer to before and after H₂SO₄ washing, respectively

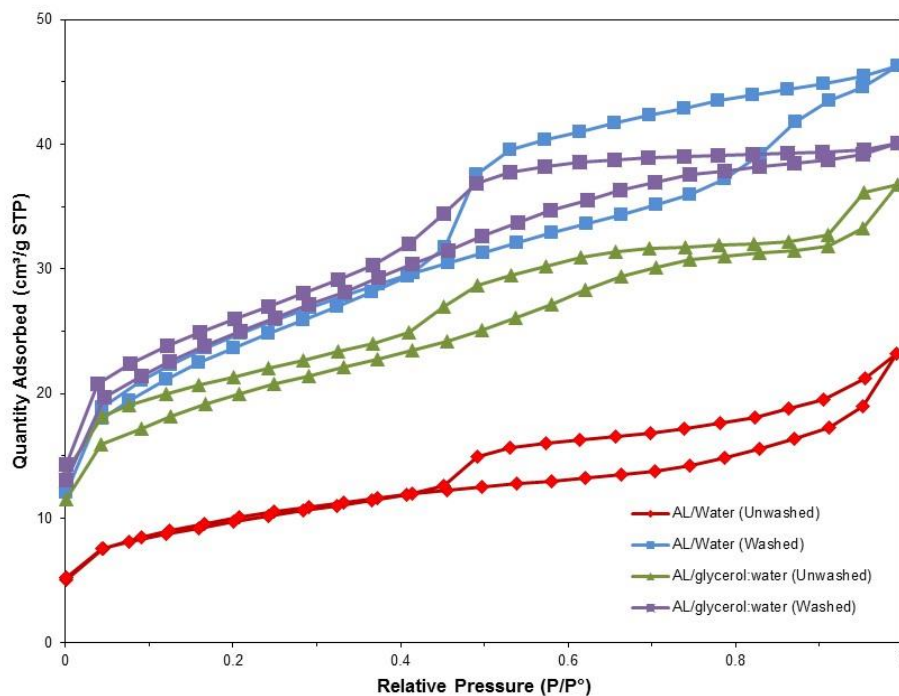


Fig. S2. Nitrogen adsorption-desorption isotherm of CFs before and after H₂SO₄ washing from AL solutions in water (lignin:water = 1:1.5 w/w) and in mixed glycerol/water solvent (lignin:solvent = 1:1.25 w/w, glycerol:water = 0.5:1 v/v)