Electrospinning of Lignin as a Carbon Fiber Precursoe

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Abstract: Electrospinning is a valuable method for polymeric to produce the nanoscale of fibres. This technique has significant attention due to its simple and efficient. To realize these more advanced functional carbon fibre, how that polymer affects the electrospinning process is essential. In this study, 10% PVA in deionised water was prepared using reflux at 25 ºC for 2 hours and mixed with 0.5, 1.0, 1.5, 2.0, and 2.5 gram of lignin. The addition of lignin to the PVA solution decreased the conductivity and increased the viscosity. The polymer solution was then electrospun with distance 13 cm, flow rate 0.2 ml/h, voltage 19 kV at 24 ºC. Using The Fourier Transform Infrared (FTIR) and Scanning electron microscopy (SEM), respectively the functional group and spun of fibre morphology were characterised. The result showed that it formed beads-fibres.

1 INTRODUCTION

Carbon fibre was produced by carbonization of carbon precursors (Gindl-altmutter et al., 2019). The different part carbon, there are carbon fibre that contain 92% of carbon based on that weight, based on pyrolysis process (Deng et al., 2013). Carbon fibre is a lightweight with a tensile frame, high strength and low density. Therefore significant benefits in development of precursors for carbon fibre, obtained renewal from biobased such as lignin. Lignin, a plant-based biopolymer, has three dimensional polyphenolic polymer and available in the plant cell walls (Chemistry, 2019; Poursorkhabi et al., 2015). Aromatic structure of lignin, supported the graphization during the carbonization process (Ago et al., 2012). There are literature study reported that applied of lignin Kraft and organosolv as a carbon fibre precursor after obtaining thermal stabilization and carbonization (Dalton et al., 2018).

Lignin-based carbon fibre offers potentially attractive manufacturing cost advantages over current technology, estimated costs on a commercial scale of around $4/Ib - $6/Ib compared to production for petroleum-based carbon fibre $10/Ib (Milbrandt & Booth, 2016).

Table 1: Cost-saving figures for carbon fibre dependent on lignin compared with traditional PAN carbon fibre.

Process Cost Category	PAN-Based Carbon Fibre Cost Estimate ($9.88/Ib)	Lignin-Based Carbon Fibre Cost Estimate ($3.71/Ib)
Precursors	$5.04	$0.50
Stabilization and oxidation	$1.54	$0.99
Carbonization and graphitization	$2.32	$1.48
Surface treatment	$0.37	$0.33
Spooling and packaging	$0.61	$0.41

The polymer should have the specifications to form a fibre, linear molecular structure, high carbon content, low polydispersity, higher molecular density, compact structure, lower crystallinity and molecular orientation (Ko, F.K., Wan, 2014).

Electrospinning was commonly employed in the manufacture of nanofibre sheets, which are applied in various fields such as Nano sensors, ultrafiltration membranes and nanocomposites (Akgul et al., 2018; Chen et al., 2014; Choi et al., 2019; Ko et al., 2015; Zhang et al., 2019).

There are parameter that affect the diameter of nanofibres including high voltage and flow rate (Abbas et al., 2016). The electrospinning fabrication

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process, the diversity of materials, the unique associated with fibres result, can be used for various application such as biomedical, drug delivery, tissue engineering, wound dressing, filter, membrane, energy and electronics (Bellan, 2008) and produced nanometre size of fibres diameters accuracy (Poursorkhabi et al., 2015).

This study aims to electrospun lignin to obtain fine fibre as a carbon fibre precursor.

2 EXPERIMENTAL

2.1 Materials

Lignin alkali, with partially soluble 13.4 wt, % loss on heating 316ºC, with pH: 6.5 (25ºC, 5% aqueous solution, d: 1.3 g/mL at 25ºC, the PVA, fully hydrolyzed (Mw approx. 60000) with viscosity 20ºC (4%; water), degree of hydrolysis ≥98.0% was purchased from Sigma Aldrich, USA. The lignin and PVA were used as received. The aqueous solutions were prepared using distilled water.

2.2 Preparation of PVA/lignin

The PVA 10% was prepared by dissolving for 4 hours 10 g of PVA in 100 mL in aquatic reflux. This process results a colorless and thick PVA solution which was mixed with amount of lignin 0.5, 1.0. 1.5, 2.0, and 2.5 g using ultrasonic (hemasonic) for 6 hours at room temperature, then calculated the conductivity and the viscosity value of the polymer solution that was analyzed.

2.3 Preparation of PVA/lignin Nano Fibre via Electrospinning

For the electrospinning process PVA/lignin solution was prepared and carried out in a horizontal electrospinning machine (syringe SP20, high voltage power supplies PS-35PV and speed controller with drum collector ESD-30S, NLI) on substrate material. The prepared 1 mL volume solutions were loaded into a 10 ml of syringe with an 18 G needle and were electrospun at 18-20 kV voltage, 0.2 mL/h feed rate of, and 13 cm tip-to-collector size. The electrospun nanofibers electrospun were then dried out for 24 hours at room temperature. Figure 1. Demonstrates the PVA/lignin cycle fabricated using electrospinning system.

Figure 1: Process of electrospinning PVA/lignin.

2.4 Characterization

2.4.1 Conductivity and Viscosity

The samples were prepared in five different concentrations of PVA/lignin and one sample of PVA aqueous as basic parameter test. Isolv AC780-Conductivity Meter determined the electrical conductivity of polymer solutions.

The viscosity solutions was determined by viscometer redwood. The step to calculated are homogenized the solution and put into viscometer tank at room temperature in *Kohlrausch* flask below of viscometer. The test repeated for three times. The viscosity of samples can determined by the formula:

$$\mu = \left(0.00260t - \frac{1.175}{t}\right)y$$

Noted:
μ = dynamics viscosity of sample (Nm/s^2)
t = times of dropped
y = density of samples (kg/m^3)
μ = (0.00260t – 1.175) y

2.4.2 Scanning Electron Microscopy

The morphology surface of electrospun was observed by scanning electron microscopy (SEM) at an accelerating voltage EHT of 20.00 kV, probe = 101 Pa and signal A = SE1. The morphology of the samples was examined with a scanning electron microscope. The samples was placed on an adhesive-backed carbon tape and secured to the specimen. The sample was sputter-coated with a thin layer of gold alloy (SC 500 emscope) to reduce the charging during analysis. that the word “Table” is spelled out.

2.4.3 Fourier Transform Infrared

The Fourier Transform Infrared Spectroscopy (FTIR) analized the functional sample groups within

the range of 4000 cm^{-1}-400 cm^{-1} with 4cm^{-1} resolution.

3 RESULT AND DISCUSSION

3.1 Viscosity

The amount of lignin added affects the viscosity of solution, because the interaction between solute and solvent in solution. The solution preparation such as concentration of component, stirring intensity, duration of stirring before mixing have important effect on the viscosity of the blends. The viscosity of polymer solutions measured at 24ºC was shown in Figure 2.

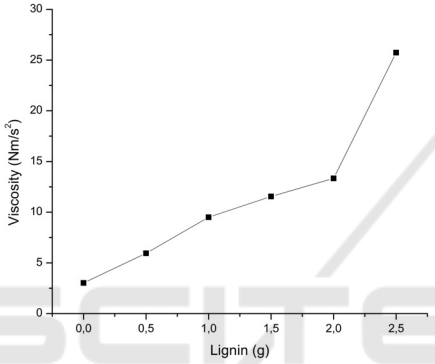

Figure 2: The viscosity of 10% PVA in deionized water/lignin.

According to figure 2, the viscosity of PVA solution with the addition of lignin. It was 3.023 Nm/s^2, and improved to 5.942 Nm/s^2, 9.497 Nm/s^2, 11.552 Nm/s^2, 13.331 Nm/s^2, 25.731 Nm/s^2, with the amount of lignin 0.5 g, 1.0 g, 1.5 g, 2.0 g, 2.5 g respectively. It might be due to the presence of macromolecular solute increased the solution's viscosity, because the large molecules affect fluid flow at great distances (Tissos et al., 2014).

3.2 Conductivity

The solution of PVA/lignin resulted different of electrical conductivity. The electrical conductivity of polymer solution has the ability to deliver an electric current, because of the ions contained in solution (Irwan & Afdal, 2016). Based on the data showed that the conductivity of PVA solution increased with the addition of 0.5 g lignin from 154.1 S/cm^{-1} to 255.5 S/cm^{-1}. However, the higher the amount of lignin the lower its conductivity. This result was the same as Mahyuni's research (Harahap, 2018). The conductivity of PVA/lignin electrospun solution was illustrated in Figure 3.

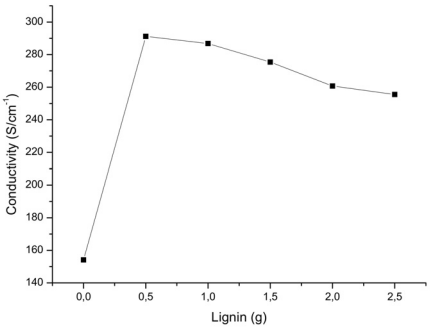

Figure 3: The conductivity of PVA 10% in deionized water/lignin.

3.3 Scanning Electron Microscopy Morphology

Figure 4 shows the morphology of the spun-fibres, with reference of the bead-fibres was produced during electrospinning. It is being the low compatibility of lignin with PVA. In addition the diameter of spun-fibres decreased with the increasing of conductivity. The electrical conductivity of polymer solutions influenced the diameter fibre electrospun. It can happen because an electric current carried by cations and anions in a colution and increased the movement of ions in solution, so the conductivity of solution increased (Irwan & Afdal, 2016). When the conductivity value is strong, the jet elongation between the tip of the needle and the collector is weaker, leading to the making of thicker fibers (Harahap, 2018). Table 2 Summarizes the diameter of the spun-fibres.

Table 2: Electrical conductivity of PVA/lignin solutions and the fibre diameter.

Sample PVA/lignin (% weight)	Electrical Conductivity S/cm^{-1}	Fibre Diameter (nm)
0	154.1	114.76
5	291.2	63.38
10	286.8	84.63
15	275.4	64.20
20	260.7	55.13
25	255.5	48.38

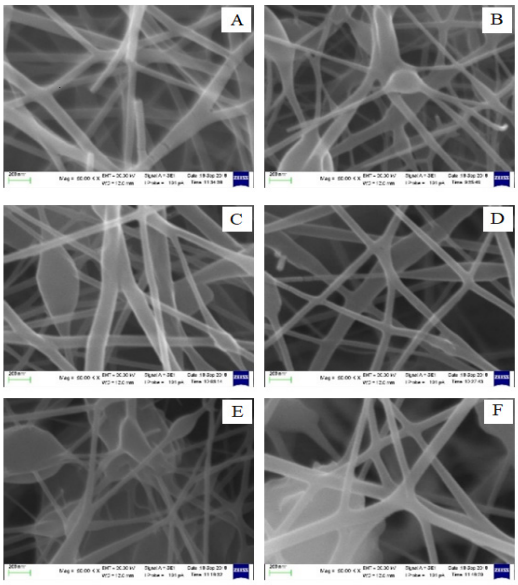

Figure 4: SEM images of PVA 10% (w/v) contained of lignin (a) 0 g (b) 0.5 g, (c) 1.0 g (d) 1.5 g, (e) 2.0 g, (f) 2.5 g.

3.4 Fourier Transform Infrared Analysis

The spectrum of FTIR lignin commercial, PVA, and PVA/lignin was illustrated in Figure 6.

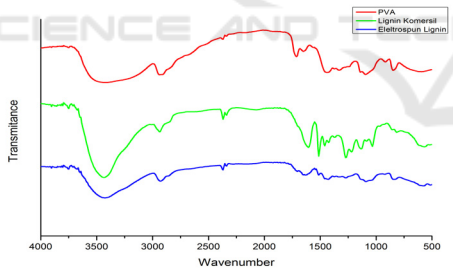

Figure 5: FTIR spectrum of lignin commercial, PVA/lignin, PVA.

The FTIR has been used to classify the groups of functions present in the materials used in this analysis. The reference disk was used to obtain the FTIR spectrum in context.

The chemical of lignin represents spectrum revealed with the literature. We can see the presence of a large peak at 3433.29 cm^{-1} linked to the stretching of O-H from the intermolecular hydrogen bonds. This peak decreased after the electrospinning lignin/PVA solution. The peaks observed at 2848 cm^{-1}-2939 cm^{-1} are respectively related to the symmetric stretching vibrational of C-H from alkyl groups. The another peak, showed at 1604 cm^{-1} indicated be assigned to the aromatic C=C stretching group, peaks at 1373 cm^{-1} related to the S=O group, and the peak at 817 cm^{-1} related to the C-O-S bonds (Rodrigues et al., 2002).

The FTIR analysis of PVA showed at 3425.58 cm^{-1} is consistent with the O-H of hydrogen bonds, the peak observed at 2916.37 cm^{-1} stretching vibrational of C-H that alkyl group, the peak at 1651 cm^{-1} C=C be assigned to the aromatic group. There are another peak of 1327 cm^{-1} is S=O group, and peak at 842 cm^{-1} can be related to C-O-S bond (Awada & Daneault, 2015).

4 CONCLUSIONS

The fabrication of lignin as a carbon fibre using electrospinning method has been successfully demonstrated. The morphology of lignin-PVA spun fibres was rough due to the inhomogeneous of lignin with the polymer solution. The diameter fibers of PVA 10% (w/v) contained lignin (0g; 0.5g; 1.0g; 1.5g; 2.0g; 2.5g are 114.76; 63.38; 84.63; 64.20; 55.13; 48.38.

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