

Preparation and Characterization of Lignin Nanofibre by Electrospinnig Technique

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Abstract

Present investigation on polymer electrospinning has emerged as a powerful technique for fabrication of nanofiber from biomaterial lignin for a wide range of applications. The electrospinning of biomaterials for fibre formation is of particular interest not only because the resources are renewable, but also because of the desirable characteristics of these bio-macromolecules, including bio-compatibility, bio-degradability and exquisite specificity. The effects of applied concentration and injection rate, tip to collector distance rotation speed of the collector and relative humidity on morphology were investigated by Scanning Electron Microscopy (SEM). Fourier transformed infrared spectroscopy (FTIR) was analysed the functional group. The thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) were investigated the thermal stability and melting behaviour of lignin and lignin nanofiber. In order to characterization, the XRD results revealed that the semi-crystalline in nature of lignin and lignin nanofiber.

Keywords: Lignin Nanofiber, Electrospinning, SEM, XRD, DSC

1. Introduction

Nanotechnology is one of the fast growing scientific disciplines due to its enormous potential in creating novel materials that have advanced applications [1]. This technology has tremendously impacted many different science and engineering disciplines, such as electronics, materials science, and polymer engineering. Nanofibers, due to their high surface area and porosity, find applications as filter medium, adsorption layers in protective clothing, etc. Electrospinning has been

found to be a viable technique to produce nanofibers [2-6].

Research activity on the electrospinning of nanofibers has been successful in spinning submicron range fibres from different polymeric solutions and melts. Fibre formation is primarily governed by the viscosity of the polymer solution and strength of the applied electric field. The viscosity of the polymer solution depends on the concentration and structure of the polymer. Often there is an upper and lower limit for polymer concentration during electrospinning [7].

On the other hand, although significant progress has been made in the electrospinning process over the past few years and the resultant nanostructures have been exploited in a wide range of applications, this simple one-step top-down nanofiber fabricating process still needs to be optimized so as to broaden its filament-forming capability over a wide range of materials and with higher nanofiber production rates [8-9].

Currently, environmental concerns have sparked interest in utilizing biodegradable and bio-derived materials in various industrial fields. Globally, lignin is regarded as a raw material with a high recovery potential, accessible from renewable sources, with low costs, a negligible pollution degree and a bountiful represent an attractive field for future industrial chemistry. Another interesting option among these potential uses for lignin is the production of nanofibers. Lignin, second only to cellulose in natural abundance, is readily available, relatively inexpensive, most abundant bio-macromolecules existing in the plant kingdom and as a precursor for nanofibers structurally appealing [10-14].

In the present investigation the preparation and characterization of lignin nanofiber (LNF) from natural resources by electrospinning technique have been attempted. A systematic study on the processing parameters that affect the formation of lignin nanofiber has been carried out.

2. Experimental

2.1 Materials and Methods

Biomaterial Lignin (Lignin protobind-1000) with density of 0.55g/cc was supplied by Greencone Environs Pvt. Ltd, Hoshiarpur Punjab-India, and Acetic acid were purchased from Sigma Aldrich, India. PEO was purchased from Sisco Research Laboratory Private Limited, India. Deionized water was used as the primary solvent.

2.2 Preparation of Lignin solution

A mixture of electrospinning solutions was prepared from lignin and PEO. All polymer concentrations are reported as w/v % (g/ml). The solutions were prepared with 0.4 % PEO, and 1.0, 1.5, 2.0, 2.5 and 3.0 wt. % lignin. Initially, lignin and PEO were dissolved in acetic acid and deionized water, while lignin was dissolved in deionized water. The two solutions were then mixed under constant stirring for 6 hours circumstances to get the preferred polymer concentrations in a 40(v/v) % acetic acid solution.

2.3 Electrospinning Process

Electrospinning was performed in a NANOMATE-S50K electrospinning setup, TSPL, India. The experimental set-up used for electrospinning process is shown in Fig.1. For electrospinning of lignin solution, the solution was taken in a 2 ml syringe to which a capillary tip of 0.56 mm inner diameter was attached. The positive electrode of the high voltage power supply is connected to the capillary wrapped with aluminium foil as shown in Fig.1. Electric voltage was optimized at 18 KV. The solutions in different concentrations were electrospun at flow rate 0.7 μ l/min and tip to collector distance

of 10 cm. Table 1.shows the details of spinning parameters that have been adopted in this experiment.

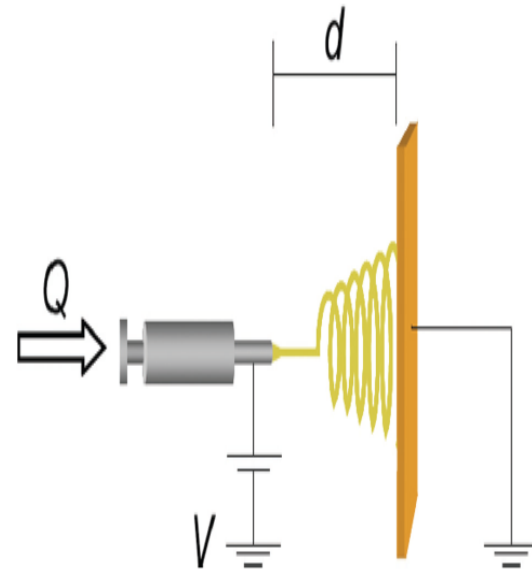


Fig. 1. Typical electrospinning setup. Q , flow rate; d , distance between plate and needle; V , applied voltage.

Polymer of High molecular weight	Lignin/PEO
Solvent	Acetic acid and H ₂ O
Injection Collector	IP607 (B)
Needle Length	Aluminium foil
Electric voltage (kV)	0.56 mm inner diameter
Capillary diameter (gauge)	18 kV
Tip to collector distance (cm)	24
Relative humidity (%)	10 cm
Temperature (°C)	40 %
Flow rate	25°C
	0.7 μ l/min

Table 1. Experimental conditions to produce lignin nanofibres by electrospinning- Parameters Values

3. Testing and Characterization

3.1 Viscosity Test

Solution viscosities were measured using a Brookfield DV-II + Pro viscometer at room temperature with a #4 spindle at 100 rpm. Each measurement had an inherent 1 % error, and three independently prepared solutions were measured to calculate an average and standard deviation. Solution surface tensions were measured using the Du Nuoy ring method with the ring attached to a microbalance at room temperature where the ring was slowly pulled out of the solution, and the surface tension being recorded just before the ring broke contact with the solution surface. Each measurement had an inherent 5 % error, and three independently prepared solutions were measured to calculate an average and standard deviation.

3.2 Scanning Electron Microscopy (SEM)

The electrospun fiber mats were sputter coated with gold and the micro to nano fibers were observed by using Scanning Electron Microscope (SEM) EVO MA 15, Carl zeiss SMT (Germany). The fibre diameters, orientation pattern of the fibres, and surface of the individual fibres were analysed using the software Scion Image or Image J. Scanning electron micrographs (SEM) are generally used to characterize electrospun nanofibers. The samples were sputtered with Au/Pd and were dried for half an hour at 70°C in vacuum, before study.

3.3 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra of lignin and lignin nanofiber were analyzed to understand the chemical interactions of functional groups by using Nicolet 6700, USA spectrometer. Each spectrum was obtained by adding 64 consecutive scans with a resolution of 4 cm⁻¹ within the range of 4000-400cm⁻¹.

3.4 X-Ray Diffraction (XRD)

XRD is a non destructive analytic technique to obtain information about the crystalline structure of a compound. XRD-7000L (3K.NOPC), Shimadzu, Japan instrument was used to analyse the sample. The nanofiber web was scanned in the range of 2θ between 1° and 80° at 295k using CuKα (λ=1.5418 Å) radiation. The nanofibrous membrane was pressed inside the sample holder, and the X-ray diffraction data were collected in the step scan mode.

3.5 Differential Scanning Calorimetry (DSC)

Using Differential Scanning Calorimetry (DSC Q 20, TA Instruments, USA), melting behaviour of lignin and lignin nanofiber samples was studied under nitrogen atmosphere. Samples of 5-10 mg weight were heated from 40 to 1000 °C at the heating rate of 10 °C / min to detect the melting characteristics of the lignin nanofiber.

3.6 Thermogravimetric Analysis (TGA)

The thermal stability of the lignin and lignin nanofiber sample was investigated under nitrogen atmosphere using thermogravimetric analysis (TGA Q 50, TA Instruments, USA). Samples ≤10 mg weight was heated from 0 to 1000 °C at the heating rate of 20 °C / minute to investigate the thermal stability of the materials.

4. Results and discussion

4.1 Viscosity

The viscosities and applied voltage of the polymer solutions with various concentrations of lignin content (1.0, 1.5, 2.0, 2.5, and 3.0 wt. %) are shown in Fig. 1. It was found to be the viscosity of the polymer solutions decreased with increasing lignin concentration. Also notice that the applied voltage increased with increasing of lignin concentrations in polymer solutions. The increase in voltage of the solution outcome in the assembly of bead and thicker nanofibers, it may be due

to the polymer solution is make longer in the high electric field [8, 9].

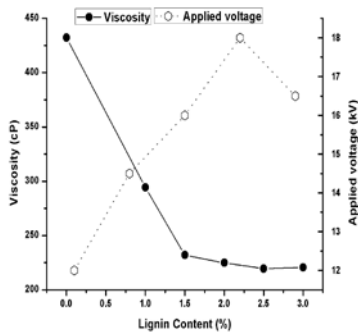


Fig. 2. Viscosity and Applied voltage vs Lignin content (%) curve

3.2 Morphology

3.2.1 Scanning Electron Microscopy (SEM) of nanofiber

The SEM images of electrospun lignin nanofiber are shown in Fig. 2. The images of 3 (a), 3 (b), 3 (c), 3(d), and 2 (e), shows the morphology studies of electrospun lignin nanofibers of 12 wt% concentration and different parameter for electrospinning process. The mean diameters of the fibers were found to be approximately 150 nm to 1µm respectively [15]. The 2.5 % lignin content fibres were found to possess the best fibre morphology out of the five samples. In the 2.5 % content lignin fibres, beading was not observed while the 1.5 % and 2.0 % lignin content had some, the 1.0 % lignin content more, and the 3.0 % lignin content fibres were thicker fiber. Thus, based on the macroscale fibre mat morphologies and microscale fibre morphologies, the 2.5 % lignin content formulation was optimal and was the focus of subsequent characterisations.

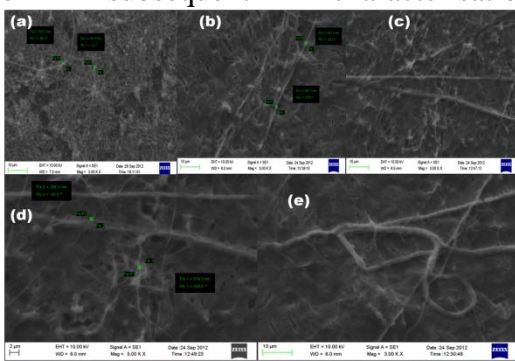


Fig. 3. SEM Images of Lignin Nanofiber:

lignin concentration of (a) 1.0 %, (b) 1.5 %, (c) 2.0 %, (d) 2.5 %, and (e) 3.0 %

3.2.2 Fourier Transform of Infra red Spectroscopy (FT-IR)

The Fourier transform infrared spectrum (FTIR) was used to identify the functionality of lignin and lignin nanofiber in the region from 500 cm⁻¹ to 4000 cm⁻¹. FT-IR spectra (Fig. 4) of lignin shows characteristic peaks such as the stretching vibration of nitrile groups (-CN-) at 2244 cm⁻¹ and the stretching vibration and bending vibration of methylene (-CH₂-) peaks at 2917 cm⁻¹ and 1448 cm⁻¹ respectively [16].

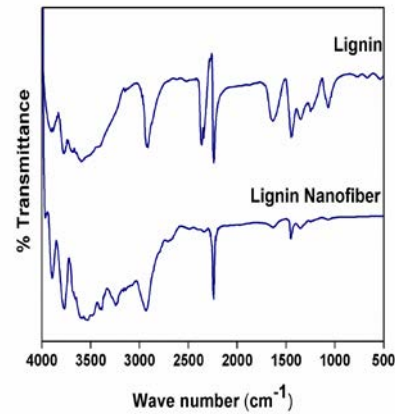


Fig.

4. FT-IR Spectrum of Lignin and Lignin nanofibers (2.5 % lignin content)

Table 2. FTIR Spectrum of Lignin nanofibers

Wave number (cm ⁻¹)	Band assignment
2244	Nitrile groups (-CN-)
2917 & 1448	Stretching vibration & bending vibration of methylene (-CH ₂ -)
1637	Carboxyl (C=O) groups
1248 and 1352	Aliphatic CH group vibrations of different modes in CH and CH ₂

Table 2 shows the FTIR Spectrum of lignin nanofiber. The peak at 1637 cm^{-1} is due to the oxidation of the as-received lignin in air, which results in the formation of carboxyl (C=O) groups [17]. The peaks at 1248 cm^{-1} and 1352 cm^{-1} are assigned to the aliphatic -CH- group vibrations of different modes in CH and CH_2 , respectively. The positions of these peaks in lignin nanofibers shift to slightly lower values due to the interaction between lignin molecules [18].

3.3 X-ray Diffraction Analysis (XRD)

XRD patterns of Lignin and Lignin Nanofibers are as shown in Fig. 5. The XRD pattern of the electrospun lignin shows a diffraction peak at $2\theta=17^\circ$. The XRD patterns of the lignin nano fibers show characteristic peaks of 2θ located at 19° , 38° , 44° , 64° , and 77° this is may be due to lignin blended with PEO [19].

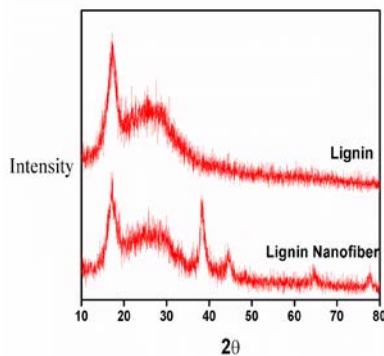


Fig.5 XRD Spectrum of lignin and lignin nanofibers

3.4 Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA)

The TGA curves for the electrospun lignin and lignin nanofibers are shown in Fig. 6. There are two obvious weight loss peaks at $305\text{-}320^\circ\text{C}$ and $600\text{-}740^\circ\text{C}$ in the TGA curves. The first weight loss is caused by dehydration in lignin and the second weight loss is due to thermo-oxidative degradation of lignin macromolecular chains [20]. It is observed in Fig. 7 that the first thermal decomposition temperature of

lignin nanofiber is around 325°C , whereas that of lignin is only 309°C . This clearly demonstrates that the lignin nanofiber system is thermally more stable than the corresponding neat lignin system [21]. This means that the incorporation of PEO into lignin offers a stabilizing effect against the decomposition.

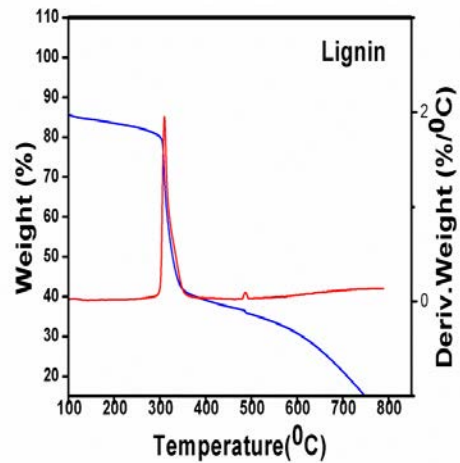


Fig.

6 TGA graph of Lignin and Lignin nanofibers

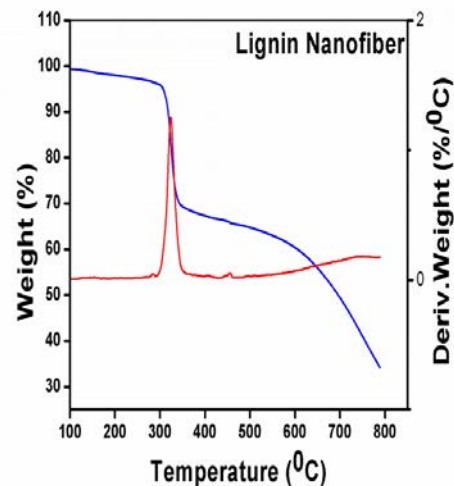


Fig. 7 DTG graph of Lignin and Lignin nanofibers

3.5 Differential Scanning Calorimetry (DSC)

Fig. 8 shows the DSC thermogram of electrospun lignin nanofibers. In lignin nanofiber the initial endotherm below 100°C is due to loss of solvent. The partial endotherm starts at above 320°C . The

major endotherm starts at above 500 °C which is due to degradation desorption of polymer backbone [22], which is also in accordance with the weight loss in TGA whereas that of the lignin is only at 310 °C and above 500 °C [23].

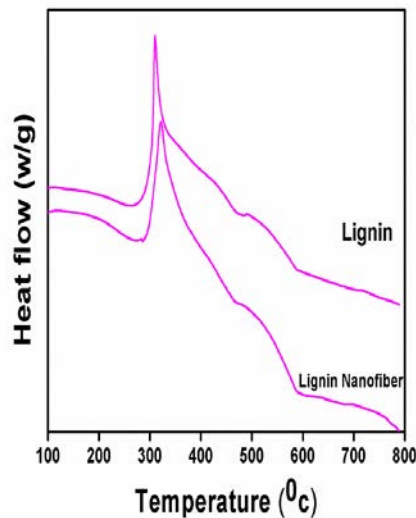


Fig.8. DSC graph of Lignin and Lignin nanofibers

4. Conclusion

Lignin nanofibers were prepared by electrospinning process. The SEM micrographs show 100 % bead free nanofibers in 2.5 % lignin content. The FTIR spectra clearly show that the positions of the peaks in lignin nanofibers shift to slightly lower values due to the interaction between lignin molecules and PEO. The XRD data clearly reveals the semicrystalline nature of lignin and the nanofibers showed diffraction peaks at $2\theta=17^\circ$ and 19° . The lignin nanofiber peaks were separated and shifted towards higher temperature when compared with that of electrospun lignin in thermal analysis which also is in accordance with the result of FTIR.

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