

## Electrospinning of Aqueous Lignin/Poly(ethylene oxide) Complexes

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**ABSTRACT:** Microfibers of kraft lignin blended with poly(ethylene oxide) (PEO) were produced by electrospinning of the solution of lignin and high molecular weight poly(ethylene oxide) (PEO) in alkaline water. Interactions between lignin and PEO in alkaline aqueous solutions create association complexes, which increases the viscosity of the solution. The effect of polymer concentration, PEO molecular weight, and storage time of solution before spinning on the morphology of the fibers was studied. It showed that after one day the viscosity dropped and fiber diameter decreased. Results from the solutions in alkaline water and N,N-dimethylformamide (DMF) with different polymer concentrations were compared. The 7 wt % of (Lignin/PEO: 95/5 wt/wt) in alkaline aqueous solution was successfully spun and the ratio of PEO in lignin/PEO mixture could be further reduced. In comparison, higher concentrations were needed to prepare a spinning solution in DMF and fiber diameters were in a much smaller range. The final target of spinning lignin is to produce carbonized fibers. Fibers spun from aqueous solutions had lower PEO content, which is a big advantage for the carbonization process as it reduces the challenges regarding melting of the fibers or void creation during carbonization. Furthermore, the larger diameter of these fibers inhibits disintegration of the carbonized fibers, which happens due to the mass loss during the process.

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### INTRODUCTION

Environmental and economic concerns related to utilizing petroleum-based materials and large availability of some biore-sourced materials are the incentives to find new approaches to replace petroleum-based materials with bioproducts. Lignin, a plant-based biopolymer, is the abundant by-product of the pulp/paper and the cellulosic ethanol industries. It is a three dimensional polyphenolic polymer and is naturally available in the plant cell walls. Percentage of lignin varies in different ligno-cellulosic materials and it can be around 15–30% of the material. Industries that require processing of cellulose have to remove lignin.<sup>1</sup> Considering the high production and demand for both paper and cellulosic ethanol, a large amount of lignin is annually produced. Current applications of lignin are limited to low-value products such as dispersing agent, emulsion

stabilizer, rheology control materials, and as a low cost fuel to produce energy.<sup>2,3</sup> However, lignin has the potential to be used in higher value products and improve the economics of the relevant industries. Lignin structure contains about 60–66% carbon that varies between lignins from different plants and isolation methods. The carbon content and chemical structure of lignin show the potential for producing carbonized materials specially carbonized lignin fibers.<sup>4–6</sup>

Melt spinning and electrospinning of lignin have been studied to produce precursor fibers for carbonization.<sup>7–19</sup> Electrospinning is a fiber spinning technology for producing nano to micro diameter fibers. The fibers are produced as nonwoven mats or they can be in the shape of aligned fiber strings. In this process polymer solution or melt is injected in an electrical field. The solution jet is stretched and elongated by electrical forces while

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the viscoelastic forces prevent it from breaking. Finally, the thin solution jet dries before reaching the grounded surface, where the fibers are collected. Electrospinning is a versatile process that can produce fibers in both random or oriented alignments and also different geometries. The other advantage is the ability to prepare blend fibers or include active materials in the fibers by dispersing them in the solution before spinning.

Pure lignin solution usually does not have the enough viscoelasticity for spinning. Therefore, it is blended with another polymer, named binder.<sup>9</sup> Solution blends of lignin and poly(ethylene oxide) (PEO), poly(vinyl alcohol) (PVA), and poly acrylonitrile (PAN) have been electrospun.<sup>11–19</sup> Most of the electrospun lignin fibers were produced from solutions prepared in N,N-dimethylformamide. Scaling up the electrospinning of solutions in organic solvents becomes complicated because of environmental and health concerns. Therefore, electrospinning of aqueous solutions is more preferable. Among water soluble polymers, electrospinning of aqueous solutions of lignin with PVA and cellulose nano-crystals have been reported.<sup>15</sup> Lignin and PVA are immiscible polymers and it limits the suitable ratio of the PVA. Schreiber et al.<sup>18</sup> reported electrospinning of aqueous solutions of sodium carbonate lignin and PEO. The maximum lignin to PEO ratio which they spun was 50/50. However, fibers with low percentage of binder polymer is preferred for carbonization process because of the lower melting point or carbon content of the binder polymers, which respectively, leads to the fusion of the fibers or pore formation.

It is known that phenolic hydroxyl groups of lignin and ether oxygen of PEO in alkaline solutions create an association induced complex formation.<sup>20–25</sup> This strong interaction suggests a promising system for electrospinning of lignin in aqueous solutions with a low percentage of binder polymer. This complex formation between PEO and lignin has been utilized in paper making, water purification, and recently bio-ethanol production process to separate particles and lignin from the process stream.<sup>23,26,27</sup> Several mechanisms have been proposed for this complex formation.<sup>28</sup> When PEO and lignin are mixed together in the presence of salts and water, the chain entanglements of PEO trap the lignin molecules and eventually the bridging of PEO chains creates an association induced complex.<sup>28</sup> Performance of PEO in bridging is dependent on its state of entanglement in solution. Fresh solutions of high molecular weight PEO contain the highest amount of chain entanglement in a nonequilibrium state and are more prone to flocculate. After passing time and with shear, PEO disentangles until reaches equilibrium state.<sup>28,29</sup> Entangled PEO forms stronger flocs than disentangled PEO.<sup>30</sup> Another important factor is the presence of a small amount of an ion that is required to dissolve the kraft lignin. Regarding the lignin/PEO ratio, addition of PEO increases the flocculation. However, increasing the lignin content reduces the flocculation due to increased amount of highly charged association complexes of PEO.<sup>30</sup> The main factors affecting the PEO solution properties are PEO molecular weight, solution temperature, shear history, and polymer solution storage time.<sup>31</sup>

In this study, the complex formation between kraft lignin and high molecular weight PEO in alkaline water and its effect on

increasing the solution viscosity is employed to prepare aqueous solutions of lignin with low percentages of PEO for electrospinning. Solution compositions were varied from the nonspinnable samples to the point that increased interactions in the solution did not allow the solution to be stretched in the electrical field. Thermal and shear history were kept the same for all of the samples and two different molecular weights of PEO were tested, a very low molecular weight and a high molecular weight. Electrospinning and fiber morphology of these samples were compared. Furthermore, the effect of storage time of solution prior to spinning on the zero shear viscosity and improving the flow properties was tested. Diameter of fibers spun from aqueous solutions at the time of preparation and one day later was compared with fibers spun from solutions in DMF.

## EXPERIMENTAL

### Materials

Softwood kraft lignin (Indulin AT) ( $\overline{M}_w=2,700 \text{ g}\cdot\text{mol}^{-1}$ ) was purchased from MeadWestvaco (USA). Its moisture content was measured before solution preparations and its average was 6 wt %. Poly(ethylene oxide) (PEO) with molecular weight of 5,000,000  $\text{g}\cdot\text{mol}^{-1}$  (PEO\_5M) and 200,000  $\text{g}\cdot\text{mol}^{-1}$  (PEO\_200k) was purchased from Sigma Aldrich. Analytical grade sodium hydroxide and N,N-dimethylformamide (DMF) were purchased from Fisher Scientific. Distilled water was used in order to prepare the aqueous solutions.

### Solution Preparation

Preliminary experiments on solubility of Indulin AT lignin in aqueous sodium hydroxide solutions with different pH showed that solutions with concentration of 0.5  $\text{mol}\cdot\text{L}^{-1}$  ( $\text{pH} > 13$ ) are capable of completely dissolving lignin.<sup>32</sup> This concentration was selected to prepare blend lignin/PEO solutions throughout the next experiments. To prepare blend lignin/PEO solutions, lignin, and PEO were first dissolved separately to assure the complete solubility of the materials. Alkaline water and distilled water were warmed to about 70°C and then lignin and PEO were gradually added, respectively. The solutions were stirred during addition of PEO to avoid agglomeration of the particles. The solutions were stirred at 70°C and 600 rpm for 2 h to completely dissolve the polymers. The equivalent volume of each solution was taken and mixed together for 15 min. The main study was on solutions with total polymer concentration of 5, 7, 9, and 11 wt/v % and two different lignin to PEO ratios of 95/5 and 97/3. Table I shows the concentration of the individual lignin and PEO solutions before and after mixing.

The solutions were stored with no further heating or stirring. It is assumed that the volume (concentration) of solutions during the experiments remained constant. This assumption was tested by keeping the same volume of water in a beaker under the same conditions from the beginning of sample preparation until the last measurement. The maximum change of volume that occurred among all the experiments was less than 2 mL (or 10%).

For preparing the solutions, a multistage magnetic stirrer/hot-plate model IKA-RT 10 was used. Three replicates of each solution were prepared.

**Table I.** Composition of the Individual Lignin and PEO Solutions Before Mixing and Final Concentrations After Mixing Equal Volume of Each Lignin and PEO Solution

Individual solutions		Composition of final blended solutions		Sample name
Lignin solution conc. (g mL <sup>-1</sup> )	PEO solution conc. (g mL <sup>-1</sup> )	Total polymer content (wt %)	Lignin/PEO ratio (wt/wt)	(Molecular weight of poly(ethylene oxide) in each sample is displayed as PEO_5M or PEO_200k)
0.095	0.005	5	95/5	5% (Lignin/PEO: 95/5)
0.097	0.003	5	97/3	5% (Lignin/PEO: 97/3)
0.133	0.007	7	95/5	7% (Lignin/PEO: 95/5)
0.135	0.0042	7	97/3	7% (Lignin/PEO: 97/3)
0.171	0.009	9	95/5	9% (Lignin/PEO: 95/5)
0.1746	0.0054	9	97/3	9% (Lignin/PEO: 97/3)
0.2134	0.0066	11	97/3	11% (Lignin/PEO: 97/3)
0.209	0.011	11	95/5	11% (Lignin/PEO: 95/5)

To compare the results of aqueous spinning and spinning of solutions in DMF, one sample with total polymer content of 11 wt/v % and lignin to PEO\_5M ratio of 95/5 was prepared in DMF. For preparing this solution in DMF, the same procedure was applied.

#### Rheological Measurement

Flow curves of the solutions were measured by Anton Paar-MCR 302 rheometer and a double gap (DG) measuring device. Applied shear rate was in the range of  $\dot{\gamma}=0.01-600\text{ s}^{-1}$  and measurements were performed at 25°C. Zero shear rate viscosity was calculated by applying the Carreau-Yasuda equation. Properties of the blended solutions were measured within 2–3 h after mixing (t1), and 24 h later (t2). For each sample the average values of three replicates are reported.

#### Electrospinning Process

Electrospinning machine NANON-01, MECC Co. (Japan) was used to spin the solutions. It has a vertical configuration and the distance between needle and collector was 22 cm. Applied voltage and feed rate were kept constant at 20 kV and 0.2 mL h<sup>-1</sup>. Temperature and relative humidity inside the machine were 30–35°C and 30–40%, respectively. After mixing lignin and PEO, mixtures were stored for at least 1 hour before spinning to provide enough time to erase the effects of applied shear during stirring.

#### Fiber Characterization

Morphology of the fibers was studied using a scanning electron microscope (SEM), Inspect S50–FEI Company. Electron acceleration voltage was 20 kV and samples were gold coated with thickness of around 20 nm before imaging. The images were analyzed by ImageJ 1.46r software. Diameter of the fibers is reported as the average of 100 measurements.

#### Analysis of the Results

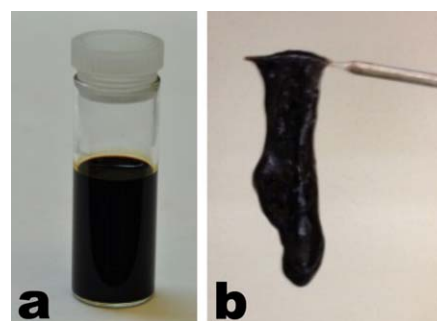
Statistical analysis of the data was performed by t-test and ANOVA using Minitab®16.2.4. A 5% level of significance was selected.

## RESULTS AND DISCUSSION

#### Solution Preparation: Effect of Total Polymer Concentration

Lignin and PEO in alkaline solutions form an association complex. Some of the factors affecting the intensity of the complex formation and its effect on the flow of the solution are composition, thermal, and shear history. As the result of these complexes, solutions become more viscose compared with the ones with the same concentration in DMF. The optimum concentration of the polymers and their ratio was determined by comparing the spinnability of the solutions. Lignin to PEO ratio was kept constant at 95/5 and the total polymer content was changed in the range of 5–50%. The PEO ratio was not increased beyond 5% based on the results of Kadla et al.<sup>7</sup> research. They found that including more PEO will hamper the carbonization process.

Electrospinning of solutions with very low concentrations was not successful because of the low interaction between the constituents and the solution just sprayed. By increasing the concentration, viscosity of the solution increased significantly to an extent that the mixture turned into a gel which did not have enough flow for spinning (Figure 1). Furthermore, solutions



**Figure 1.** (a) Solution of lignin and PEO\_5M prepared for spinning. (b) The gel formed by mixing high concentrations of lignin and PEO\_5M. The whole mixed solution turned into a gel. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

with high viscosities resist to bending instability during spinning. Therefore, higher electrical forces are required to overcome the viscoelastic forces.<sup>33</sup> It results in larger fiber diameter at a constant voltage. Solution jets with extremely high viscosities cannot go through the appropriate path of electrospinning and connect the needle and the collector. The second limiting factor for increasing the concentration is the lignin solubility in alkaline solution. As lignin and PEO solutions were prepared separately and then mixed, increasing the lignin concentration is limited by its interactions with the alkaline solution. Solutions with high percentages of lignin (approximately above 30 wt % lignin) needed heating to stay in the liquid form. This is probably due to hydrogen bonding between lignin and the alkaline solution.<sup>34,35</sup>

Solution preparation conditions such as concentration of the components, temperature, stirring intensity, and duration of stirring before mixing have important effects on the viscosity of the blends and the extent of gelation.<sup>28</sup> Increased stirring times of solutions of high molecular weight PEO disentangles the chains until it reaches equilibrium.<sup>29</sup> However, complete disentanglement is not required for electrospinning as chain entanglements increase the interactions between lignin and PEO and therefore improve the solution elasticity for the spinning. However, it should be noted that a high amount of entanglement may result in an excessive interaction which eventually creates a gel which does not have enough flow for spinning. In these cases, increased shear and temperature will reduce the elasticity of the solution. Another important parameter is the alkalinity of the solution. Increasing the pH value reduces the association of lignin molecules. For the current experiments, thermal and shear history were kept constant for all the samples. Reducing the temperature and shear increases

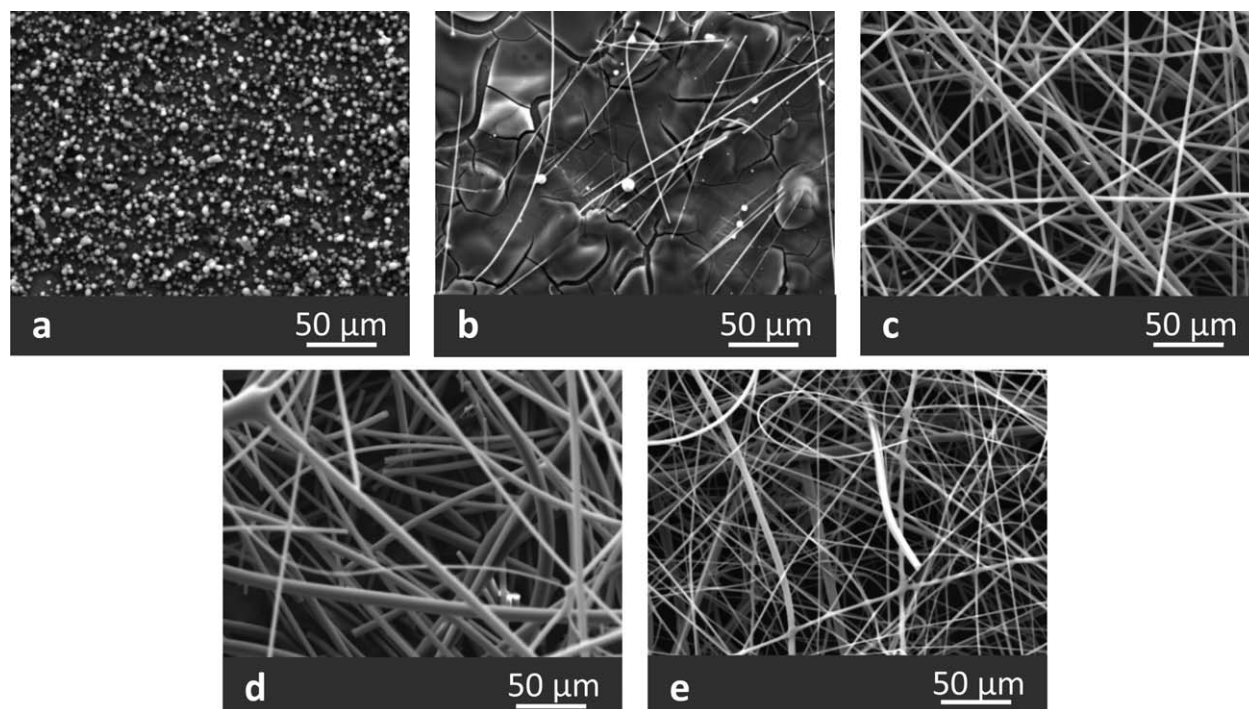
the probability of gelation. By applying the procedure outlined in the experimental section, at total concentration more than 11%, mixed solutions turned into a highly elastic gel that did not have enough flow for spinning [Figure 1(b)]. Therefore, from these preliminary observations, the total polymer content of 5, 7, 9, and 11% were selected for electrospinning.

#### Solution Preparation: Effect of Lignin to PEO Ratio

To determine the lignin to PEO\_5M ratio, total polymer concentration was kept at 10% and solutions with lignin to PEO\_5M ratios of 99/1 to 95/5, 90/10, and 85/15 were tested. Solutions were stored for 4 days before spinning. The reason for storing was to find a concentration, which is still spinnable after storing for a few days. Solutions with lignin/PEO\_5M ratios of 90/10 and 85/15 turned into a gel because of high PEO content. Figure 2 shows the SEM images of spun solutions with 10% polymer and varying ratios of lignin/PEO\_5M between 99/1 and 95/5. Solution with 1% PEO\_5M sprayed and created particles. The 2% PEO\_5M could make very short fibers and the jet broke to create particles. Solutions with 3–5% PEO\_5M made continuous smooth fibers. However, increasing the PEO\_5M content increases the viscosity of the solution and therefore the diameters increased. From these observations lignin/PEO\_5M ratios of 95/5 and 97/3 were selected for the rest of the studies.

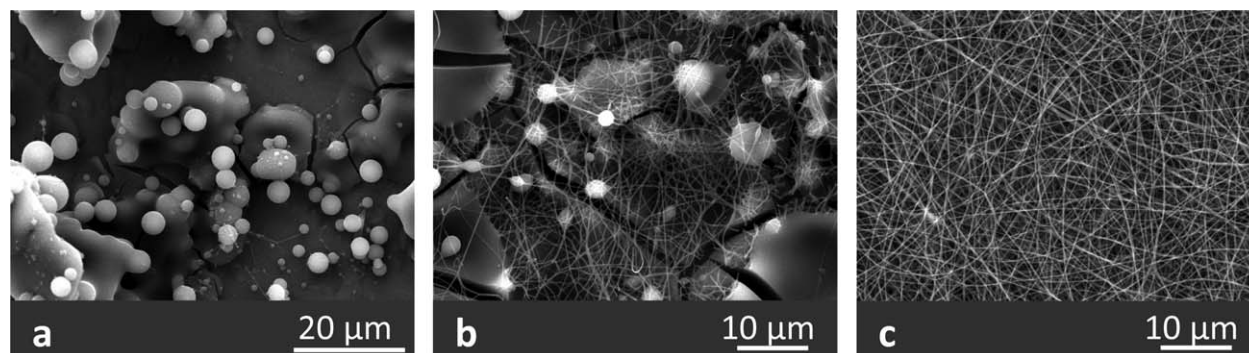
#### Solution Preparation: Effect of PEO Molecular Weight

Reducing the molecular weight of PEO decreases the viscosity of the solution and gel formation occurs at higher concentrations. In this study, a very low molecular weight of PEO (PEO\_200k) was tested. Figure 3 shows the SEM images of spinning of solutions with 10% polymer and three different PEO\_200k ratios. Solution with 10% (lignin/PEO\_200k: 85/15)



**Figure 2.** Effect of different lignin to PEO\_5M ratios. (a) 10% (Lignin/PEO\_5M: 99/1), (b) 10% (Lignin/PEO\_5M: 98/2), (c) 10% (Lignin/PEO\_5M: 97/3), (d) 10% (Lignin/PEO\_5M: 96/4), (e) 10% (Lignin/PEO\_5M: 95/5). (Sample names were explained in Table I).





**Figure 3.** Effect of low molecular weight PEO. (a) 10% (Lignin/PEO\_200K: 95/5), (b) 10% (Lignin/PEO\_200K: 90/10), (c) 10% (Lignin/PEO\_200K: 85/15). (Sample names were explained in Table I).

could produce microscale fibers, while reducing the PEO ratio increased the formation of particles, which were the result of spraying and at 5% PEO, no fiber was produced.

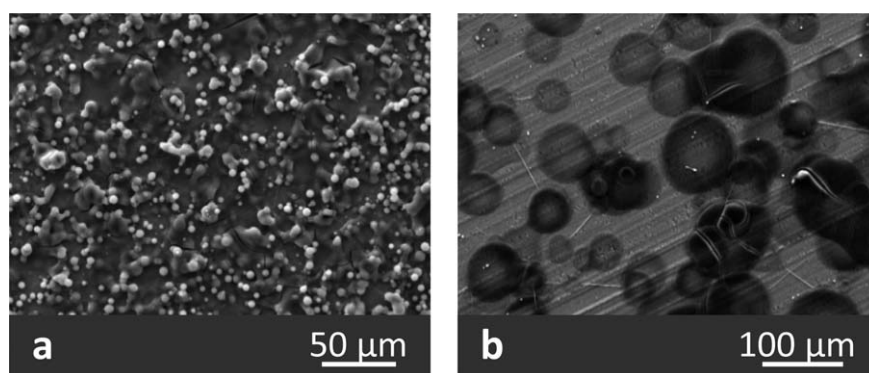
Figure 4 shows the effect of increasing the total polymer content to 11% and 15%, whereas keeping the lignin/PEO\_200k ratio constant at 95/5. It did not improve the fiber formation and the solution just sprayed. This shows the solution did not have enough elasticity. Low-molecular-weight PEO has shorter chains with lower efficiency in bridging the polymers<sup>22</sup> so a larger amount of PEO\_200k was required for successful spinning. Increasing the PEO concentration was accompanied by increasing lignin concentration to get the same ratios. Further increasing the concentration was limited by difficulties in dissolving high concentrations of lignin in alkaline solutions. Lignin interacts with the solvent and upon increasing the amount of lignin in solution these interactions resulted in solidification at room temperature. Since electrospinning is performed at room temperature, it was not feasible to heat the solution to a liquid. Therefore, 15% of lignin/PEO\_200k was the highest total concentration that could be studied.

### Electrospun Fiber Morphology

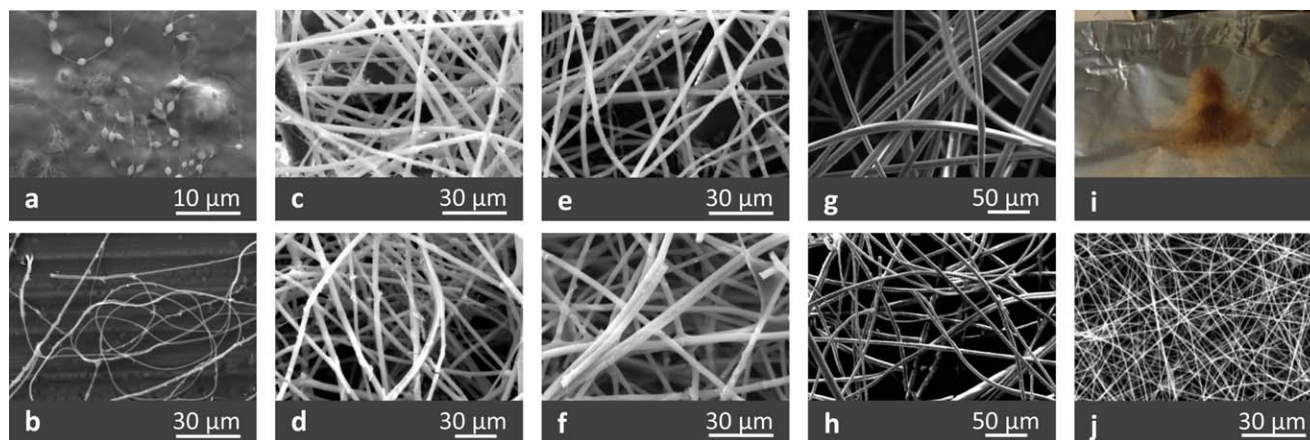
After the preliminary experiments to find the range of concentrations, the effect of solution concentration and lignin/PEO ratio on the fiber morphology and diameter was studied. These experiments were performed using PEO with high molecular

weight ( $5,000,000 \text{ g mol}^{-1}$ ). Total polymer content was selected to be 5, 7, 9, and 11%. For each concentration two ratios of 95/5 and 97/3 were tested. The results are shown in Figure 5. Except for 5% polymer content, other ratios could be spun into fibers. Solutions with 11% polymer had higher viscosity and the jet could not go through a large bending path. Therefore, the fibers were stacked on each other on a small area [Figure 5(i)]. Further increasing the total polymer concentration is limited because of the increase in solution resistance to stretching in the electrical field. As a result, a continuous direct solution jet comes out of the needle and connects to the collector, creating a short circuit that finally burns the polymer with created electrical sparks.

To compare the results of electrospinning aqueous and organic solutions of lignin, a solution in DMF with the highest concentration that was made in water was tested [Figure 5(j)]. Diameter of the fibers spun from aqueous solutions was larger than DMF solutions. Figure 7 shows a box plot of fiber diameter distributions with respect to the solution composition. With increasing PEO\_5M content and also total polymer concentration, the fiber diameter increased. Because of higher concentrations, more material is pulled out of the needle resulting in higher diameters. Furthermore, the higher concentrations results in higher viscoelasticity and a shorter path for the jet before reaching the collector. Therefore, the jet elongation is reduced and fiber diameter increases.



**Figure 4.** Effect of increasing the total polymer concentration of solutions of (lignin/PEO\_200k: 95/5). (a) total polymer = 11%, (b) total polymer = 15%. (Sample names were explained in Table I).



**Figure 5.** Electrospinning of (Lignin/PEO\_5M) aqueous solutions at the same preparation day (at time: t1). Only sample (j) was a solution in DMF. (a) 5% (lignin/PEO\_5M: 97/3), (b) 5% (lignin/PEO\_5M: 95/5), (c) 7% (lignin/PEO\_5M: 97/3), (d) 7% (lignin/PEO\_5M: 95/5), (e) 9% (lignin/PEO\_5M: 97/3), (f) 9% (lignin/PEO\_5M: 95/5), (g) 11% (lignin/PEO\_5M: 97/3), (h) 11% (lignin/PEO\_5M: 95/5), (i) picture of collected fibers of 11% (lignin/PEO\_5M: 95/5), (j) 11% (lignin/PEO\_5M: 95/5) in DMF. (Sample names were explained in Table I). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

The next studied parameter is the effect of storing time. High molecular weight PEO in the solution state relaxes over time which reduces its chain entanglements until it reaches equilibrium. Under stirring condition, it takes up to 24 h to reach equilibrium.<sup>28</sup> The extensional flow behavior of PEO solutions especially at entrance and exit of capillaries strongly depends on the state of chain entanglements. Fresh solutions contain polymer clusters which resist the deformation but entangled chains can be stretched.<sup>28</sup> In the case of lignin/PEO complexes, this relaxation results in the reduction of solution elasticity. In this study, the solutions were stored at room temperature ( $\sim 25^{\circ}\text{C}$ ) without stirring for 24 h. The electrospinning results showed the effect of storage time and polymer disentanglements on the fiber diameters. The SEM images of the fibers spun from the solutions after 24 h (t2) are shown in Figure 6. Solutions with 5% polymer at t2 showed the same result as time t1, that is, it could not be spun. The other solutions were spun into continuous fibers. Figure 7 compares the boxplot of fiber diameter distribution at both time t1 and t2. In both times, with increasing PEO content, the diameter increases. At time t2 the fiber diameter distribution as well as its average reduced for all the samples compared with time t1. This reduction was bigger for samples with higher PEO\_5M content. At time t2, PEO is relaxed and it has less entanglement so the solutions are more uniformly stretched. It is tested by measuring the zero shear viscosity of the solutions.

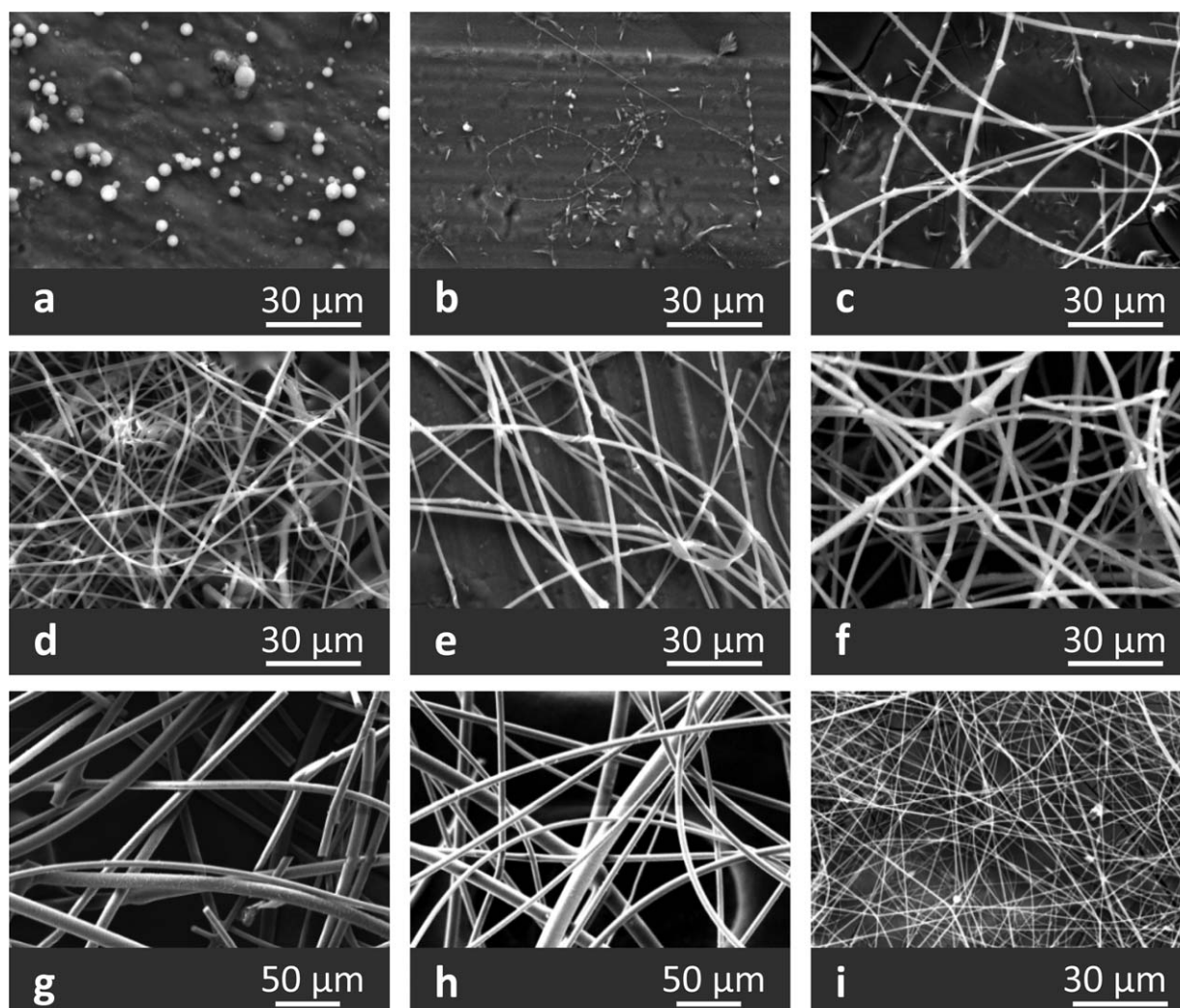
Zero shear viscosity of the solutions was measured at both time t1 and t2. It is a measure of viscoelasticity of the solutions and is one of the parameters affecting the electrospinning and diameter of the fibers. Figure 8 shows the average of fiber diameter and zero shear viscosity of different solutions at time t1 and t2. At time t1, the viscosity increases with increasing PEO content. The same trend is observed at time t2 but the viscosities are lower compared with time t1. The PEO bridging complex flattens over time thus weakening the bond.<sup>30</sup> Average fiber diameters follow the same trend as solution viscosity but because of

other factors they do not exactly follow the viscosity. Solution with 11% (lignin/PEO\_5M: 97/3) has an unusual increase in both the viscosity and fiber diameter. This could be due to residual shear history of the solution before spinning. The lignin/PEO solutions are highly sensitive to shear. At high concentrations which are close to gel formation, excessive stirring the solution increases the viscosity and it reduces the stretching of the solution during the spinning. As the result, the fiber diameters increase. Another reason for the different behavior of 11% solution could be the temperature drop during mixing the lignin and PEO. At temperatures above  $40^{\circ}\text{C}$  the efficiency of complex formation is reduced.<sup>22</sup> All the blended solutions were prepared at temperatures slightly above  $40^{\circ}\text{C}$ . It is possible that for this sample temperature fluctuation caused more complex formation and therefore higher viscosity occurred.

The solution prepared in DMF had lower viscosity compared to the same composition made in water. This sample could be spun and made continuous fibers with much thinner diameters. In another comparison, although solution in DMF had higher viscosity compared with solutions in water with lower concentrations, the spun fibers from DMF had lower diameter and narrower diameter distribution. This can be attributed to the effect of the solvent. This is probably the higher dielectric constant of DMF which enables more stretching of the solution compared with the aqueous solutions.

The changes in fiber diameter and also the solution viscosities were analyzed using statistical methods. The results of t-test analysis with significance level of 5% showed that there is a significant difference between the average fiber diameters between time t1 and t2. ANOVA was used to find out whether there is any difference in average fiber diameters between different PEO concentrations for samples spun at time t1. The results showed that there is a significant difference between diameter of fibers spun from solutions with 11% (Lignin/PEO\_5M: 95/5), 11% (Lignin/PEO\_5M: 97/3), and 11% (Lignin/PEO\_5M: 95/5) spun in DMF. These samples are also significantly different with 9%

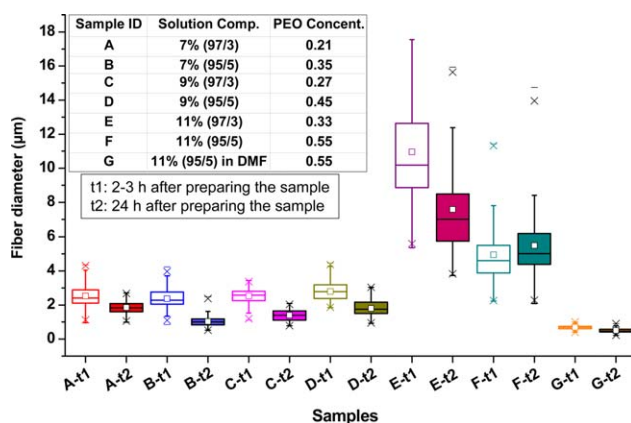




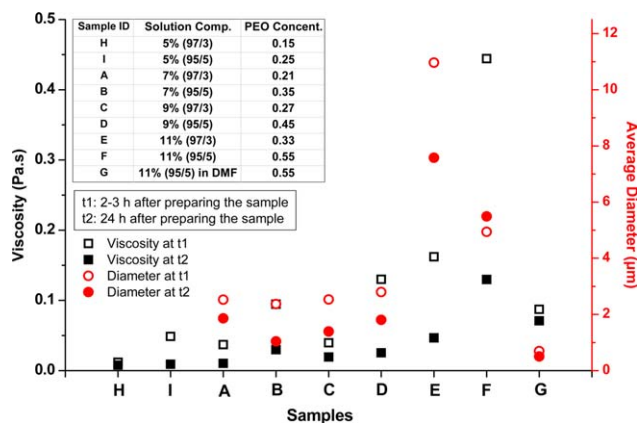
**Figure 6.** Effect of time on spinning of (Lignin/PEO\_5M) aqueous solutions after 24 h storage (fibers spun at time t<sub>2</sub>). Only sample (i) was spun from solution in DMF. (a) 5% (lignin/PEO\_5M: 97/3), (b) 5% (lignin/PEO\_5M: 95/5), (c) 7% (lignin/PEO\_5M: 97/3), (d) 7% (lignin/PEO\_5M: 95/5), (e) 9% (lignin/PEO\_5M: 97/3), (f) 9% (lignin/PEO\_5M: 95/5), (g) 11% (lignin/PEO\_5M: 97/3), (h) 11% (lignin/PEO\_5M: 95/5), (i) 11% (lignin/PEO\_5M: 95/5) in DMF. (Sample names were explained in Table I).

(Lignin/PEO\_5M: 95/5), 9% (Lignin/PEO\_5M: 97/3), 7% (Lignin/PEO\_5M: 97/3), 7% (Lignin/PEO\_5M: 95/5). The samples in the latter group (7 and 9% solutions) are not different from each other. Almost the same trend is observed in the fibers spun at time t<sub>2</sub>. For viscosities at time t<sub>1</sub>, solution with 11% (Lignin/PEO\_5M: 95/5) is significantly different than all other samples. Solution with 11% (Lignin/PEO\_5M: 97/3) is significantly different with 7% (Lignin/PEO\_5M: 97/3) and 5% (Lignin/PEO\_5M: 97/3). At time t<sub>2</sub>, almost the same trend is observed.

Another interesting result is regarding the collection of the fiber mats. Fibers spun from DMF solutions tend to stick to the aluminum foil collector. Spinning of high solution concentrations for several hours is required in order to separate and collect the fiber mat. In comparison, the fibers spun from the aqueous solutions had lower tendency to adhere to the foil. At the beginning of spinning, newer fibers were collecting on top of the



**Figure 7.** Diameter distributions of fibers spun from solutions with different (Lignin/PEO\_5M) concentrations and at times t<sub>1</sub> and t<sub>2</sub>. The table shows the wt % of PEO\_5M in each solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**Figure 8.** Effect of time on changing the solution viscosity and average diameter of spun fibers for solutions of (Lignin/PEO<sub>5M</sub>). The table shows the wt % of PEO<sub>5M</sub> in each solution. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

other fibers rather than spreading on the foil. Longer spinning for about 1 h, depending on the solution concentration, made a fiber mat which could be separated from the foil.

## CONCLUSIONS

Chain entanglements and formation of complexes between lignin and PEO in alkaline solutions were used to obtain solutions with enough elasticity for spinning into continuous fibers. The results showed that low molecular weight PEO was not able to produce enough entanglement and association with lignin to increase the viscosity suitable for spinning. Storing the samples reduced the solution viscosity and as a result reduced the fiber diameter and its distribution. With increasing PEO concentration, both the viscosity and fiber diameters increased. However, these properties decreased after storing the solutions for 24 h. Statistical analysis was applied to find significant differences between the results. Increasing the aqueous solution concentration was limited by flow properties of concentrated solutions. The highest composition which was made in aqueous solvent was 11% (Indulin AT/PEO<sub>5M</sub>: 95/5). Solution with the same composition was also prepared in DMF. It had lower viscosity and spun fibers had smaller average diameter compared with the aqueous solution. Utilizing alkaline solutions to dissolve lignin and PEO for spinning has advantages such as less material required to create the fibers, ease of separation of fiber mats from the collecting foil, and utilizing a greener and cheaper solvent. The above results were obtained for solutions which were stirred for 2 h at 70°C and 600 rpm before mixing. Increasing the stirring time, intensity, temperature, or storing the mixed solutions for longer periods of time will reduce the strength of the interactions and gel formation and therefore makes it possible to increase the polymer content or reduce the fiber diameters. These electrospun lignin fibers can be further carbonized to produce lignin based carbon fibers.

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