Synthesis of soy protein–lignin nanofibers by solution electrospinning

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Abstract

Nanofibers were produced by electrospinning aqueous alkaline solutions containing different mass ratios of soy protein and lignin in the presence of poly(ethylene glycol) coadjuvant, all of which presented shear thinning behavior. SEM revealed that the addition of polyethylene oxide as a coadjuvant indeed facilitated the formation of defect-free fibers whose diameter increased with lignin concentration, in the range between ≈124 and ≈400 nm. Favorable interactions between lignin and soy protein were identified from data provided by differential scanning calorimetry. In addition, an increased hydrogen bonding and the loss of secondary structure of the proteins as the lignin concentration increased were observed from the disappearance of amide II (~1500 cm⁻¹) and III (~1400–1200 cm⁻¹) bands and a red shift of amide I band in the FT-IR spectrum. The unfolding of the protein contributed to a better interaction with lignin macromolecules, which further improved the electrospinning process. It is concluded that mixtures of lignin and soy proteins, two major renewable resources with interesting chemical features, are suitable for the development of composite sub-micron fibers.

1. Introduction

Interest in the development of environmentally friendly materials has sparked the use of renewable precursor polymers and green manufacturing techniques. In the area of fiber formation, the time-renowned electrospinning technique allows production of continuous filaments from the nanometer to micrometer scale [1–6]. During the process, a polymer solution is pumped through a nozzle at the same time that a high voltage is applied between the nozzle and a metallic collector. The voltage induces electrostatic repulsion that stretches the liquid droplet at the tip of the nozzle forming a conical shape, the so-called Taylor cone. When the electrostatic repulsion overcomes the surface tension of the solution, the liquid is expelled from the nozzle as a jet that forms the fibers. The high surface area of fibers produced by electrospinning makes them ideally suitable for a wide variety of applications including tissue engineering, cosmetics, wound dressing, filtration media, catalysis, nanosensors and military protective clothing [2,3,6]. The use of natural polymers alone or in combination with synthetic polymers to produce nanofibers by electrospinning has gained increased attention over the last decade; some of the polymers studied include cellulose acetate [7–9], collagen [10], hyaluronic acid [11], chitosan [12,13], poly(lactic acid) (PLA), silk proteins [5,6], poly-ε-caprolactone [14], cellulose [15–17], soy proteins [18,19], and lignin [20–22].

Lignin, the most abundant non-cellulosic polymer on earth, [23] is a complex aromatic (phenolic) macromolecule present in the cell wall of plants; it is composed of three main phenylpropanoid monomers or precursors: coniferyl, sinapyl and p-coumaryl alcohol [24]. Uses of lignin different than energy co-generation include those that take advantage of its chemical features as well as its physical and thermal properties when combined with other (bio)polymers; for example, in composite materials. Lignin has been studied for a variety of applications, from dispersants [23], and adhesives to the production of composite materials (phenolic resins) and carbon fibers [23,25–28].

The production of lignin fibers (micro and nanofibers) by the electrospinning technique has been reported recently [20–22,25,26,29]. The addition of polyethylene oxide [20] or polyvinyl alcohol [21,22] coadjuvants has been noted to improve intermolecular interactions, which leads to uniform fibers.

In contrast with lignin, soybean proteins display a thermoplastic behavior and are among the most investigated renewable materials for non-food applications, including wood adhesives,
films for food packaging, composites, bio-based plastics and paper coatings [30,31]. Several approaches have been studied to produce “green materials” from soybean proteins mixed with other polymers, including poly (ethylene oxide) in films [32] or electrospun fibers [18,19]. It was shown that PEO addition enhances fiber formation during electrospinning at concentrations up to 0.8 wt% in alkaline aqueous solution in the presence of a nonionic surfactant (Triton X-100). This synergistic effect was attributed to the increase in viscosity and reduction of electrical conductivity [18]. It has been suggested that PEO interacts with protein molecules and its amino acid residues through hydrogen bonding, hydrophobic, and ionic interactions [33]. Organic solvents have also been used to dissolve soy protein isolates to make them suitable for electrospinning. For instance, 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) was used as a solvent for the production of soy isolate-PEO fibers by electrospinning and similarly for the case of aqueous solutions, blends of soy isolate-PEO in HFIP produced defect-free hydrophilic fibers, indicating good compatibility between PEO and soy proteins [19].

Blends of soy protein and polyvinyl alcohol (PVA) produce electrospun nanofibers [34]; PVA exhibits similar performance to that of PEO by facilitating uniform fibers with a total polymer concentration of up to 13 wt-% in alkaline aqueous solution, which helps denature the proteins. Finally, lignin has been studied in blends with soy proteins to produce composite materials [28,35] and also as a filler in soy protein plastics [36,37]. The main objective in this study was to evaluate the feasibility of using the predominant protein in soy, glycinin (G) as well as soy protein isolate (I) and flour, to produce sub-micron fibers from aqueous solutions containing dissolved lignin. We found that the interactions of glycinin with lignin and cellulose were quite different compared to those with β-conglycinin, the other dominant protein in soy [38,39]. Therefore a question that emerges is if the quality and characteristics of soy-based fibers are affected by the detailed composition of the component proteins. It was expected that such would be the case given the reported affinity between glycinin and lignin [39]. This will lead to the production of the composite electrospun fibers as facilitated by such favorable intermolecular interactions. To the best of our knowledge this is the first time that electrospinning of mixtures of soy protein and lignin has been reported. Thus, a leading hypothesis in this work is that given the favorable dynamics of interaction blends of lignin and soy proteins can produce defect-free fibers. Because both biopolymers contain suitable functional groups for chemical modifications, the produced electrospun mats can be subjected to further chemical treatment such as crosslinking, which can result in the development of new, functional bio-based fibers.

2. Experimental

2.1. Materials

Kraft lignin (alkali lignin, low sulfur content), polyethylene oxide (Mw = 400,000) and acetonitrile were purchased from Sigma Aldrich (St. Louis, MO). Sodium hydroxide standard solution (0.1 N) was purchased from Fisher Scientific. Soy protein isolate (I) (Profam 974) and soy flour (7B flour) were obtained gifts from Archers Daniel Midland. Soy glycinin (G) was obtained by fractionation of defatted soy flour as described in our previous work [38]: the reported molecular weight of glycinin is 340–350-KDa [40,41].

2.1.1. Electrospinning solutions

Blends of soy protein, lignin and PEO were prepared using a 10 vol-% acetonitrile in 0.1 N sodium hydroxide aqueous solutions. After evaluation of different polymer concentrations, it was found that 8 wt-% total polymer concentration in solution produced uniform fibers. In addition, this concentration allowed a wide range of suitable mixing ratios for soy protein and lignin while keeping the amount of polyethylene oxide (PEO) in the nanofibers fixed at 10 wt-% based on the total mass of the macromolecules (Table 1).

Initially, a solution of polyethylene oxide was prepared and left under stirring overnight for complete dissolution, then appropriate amounts of protein were added slowly to the PEO solution while stirring and kept under stirring for at least four hours until complete dissolution of the protein. Following, lignin powder was added slowly and the resultant mixture was kept for four more hours under vigorous magnetic stirring.

2.2. Characterization

Soy glycinin (G) and isolate (I) were used to produce sub-micron fibers. Different protein (G or I):lignin ratios were used with a fixed amount of polyethylene oxide, which served as coadjuvant in the spinning process. Each solution was loaded into a disposable plastic syringe (10 ml) with a 22 gauge needle. The needle was connected to the positive terminal of a voltage generator (Glassman High Voltage, Series EL) and a 15-cm diameter aluminum plate collector covered with a thin aluminum foil, connected to the negative electrode of the power supply (ground). An operating voltage of 15 kV, polymer solution flow rate of 8 μl/min (computer-controlled syringe pump) and working distance of 22 cm (needle tip to collector) were used. Electrospinning was run at room temperature and humidity between 30% and 40%.

The morphology of the electrospun fibers collected as mats was examined using a field emission scanning electron microscope (FE-SEM, JEOL, 6400F) operating at 5 kV and working distance of 22 cm. The samples were left overnight at 40 °C in a vacuum oven to remove any residual moisture present. DSC thermograms were obtained by removing first the moisture and thermal history of the samples, equilibrating at 40 °C for 1 min and heating to 105 °C, keeping isothermal conditions for 12 min. The heating cycle was carried out after cooling to 40 °C followed by equilibration during 3 min and heating up to 200 °C. All data were collected in the second heating cycle. A ramp of 10 °C per minute was used for all heating/cooling cycles. All experiments were run using hermetic pans with a small hole intentionally open to purge water vapor generated from the moisture of the samples.

Fourier Transform Infrared Spectroscopy (FT-IR) measurements were carried out on a Nicolet Nexus 670 FT-IR (ThermoScientific)
in transmittance mode with a wavenumber resolution of 4 cm\(^{-1}\) and using 64 scans per sample. The fiber mats were dried overnight in a vacuum oven at 40 °C before grinding them with potassium bromide to produce the FTIR pellets (1 mg per 100 mg KBr).

The viscosity of the precursor solutions was determined at 25 °C by using an AR2000 rheometer (TA Instruments, New Castle, DE). A 40 mm steel plate geometry was used (parallel plate configuration) following a continuous flow procedure, the shear rate was ramped from 0.1 to 1000 s\(^{-1}\). The surface tension was measured using a DCA-312 Cahn balance (Thermoscientific), and the conductivity was measured at room temperature using a conductivity meter (Corning Inc., model 441).

The initial, static water contact angles of the electrospun mats were measured with a Phoenix 300 system (SEO Corp., Korea). Droplets of 4 μL volume were deposited on a small piece of the fiber mat (2 × 2 cm). The images of the sessile drop were acquired using the “Image J” software (National Institutes of Health, U.S.) with imaging codes (Drop Snake, Biomedical Imaging Group, Ecole Polytechnique Fédérale de Lausanne (EPFL)). [42] The reported results were averages of triplicates for each substrate.

3. Results and discussion

3.1. Rheological behavior of electrospinning precursor solutions

At the polymer concentrations considered here, all samples exhibited shear thinning behavior, which is more remarkable for suspensions with large amounts of protein (Fig. 1). However, the flow curves for solutions with glycycin and soy isolate followed different trends, as observed in Fig. 1a. The apparent viscosity of solutions containing glycycin (G) decreased as the amount of protein decreased (up to 50% protein) then it increased for samples containing less protein (33% and 22%). The apparent viscosity values followed the order (from largest to smallest values): G1 > G4 > G3 > G2, for the entire range of shear rates used. For soy protein isolate (I) the trend is slightly different: at low shear rates (below 10 s\(^{-1}\)) the apparent viscosity followed the trend I1>I3>I2>I4 and at high shear rates the trend is I1 > I2 > I3 > I4. The high viscosity of precursor solutions 11 and 13 at low shear rates may be due to the presence of microstructures (protein clusters) as a result of protein aggregation in solution, the latter effect is discussed further below in light of interfacial interactions.

3.2. Fiber morphology

The SEM images of fibers prepared from soy glycycin 11S (G) and soy isolate (I) at different ratios can be observed in Fig. 2. Uniform fibers were obtained from electrospinning soy proteins and lignin; however, a few (and small) fiber engrossments were observed for samples obtained from the highest protein:lignin ratios (78% protein content). This can be explained by the properties of these electrospinning solutions: G1 and I1 precursor solutions were the most viscous and also had the lowest conductivity (see Table 1). The uniform morphologies generally observed in the electrospun fibers indicated favorable interactions between lignin and the soy proteins; these interactions are enhanced via hydrogen bonding by the presence of carboxylic groups in both components. There is an increase in fiber diameter for both polymer composite blends (G1–G4 and I1–I4); an increase in fiber diameter is clearly observed as the lignin loading is increased (Fig. 2 and Table 2).

In order to evaluate qualitatively the interactions of lignin with proteins in the blend, films casted from each solution were prepared and imaged (SEM) in cross sections after cryo-fracture (Fig. 3). No micro phase separation was identified in the films produced from blends with 78% (G1) and 50% (G2) protein. However, some small aggregates (clusters) were formed when the protein concentration was reduced (G3 and G4). A similar effect was observed in blends with soy isolate (I), but in this case small aggregates already appeared in the sample containing 50% protein. One can speculate that these observations are ascribed to the size and shape of the macromolecules because compared with lignin, globular proteins almost certainly possess a larger effective volume. In systems with high protein loading (78% protein) lignin molecules have a considerable mobility in the blend, because of their relatively smaller size. When lignin is the major constituent (22% protein content) the proteins are embedded in the lignin matrix; it is possible that their molecular mobility is restricted because of their larger size. In addition, it can be speculated that in the precursor solution conditions the unfolded protein molecules expose their hydrophobic amino acids, which improves further the interactions with lignin; meanwhile, the hydrophilic amino acids self-exclude from the blend, contributing to cluster formation. The formation of hydrophobic clusters of soy protein in alkaline conditions (pH 9.5) has been reported, a phenomenon that is dependent on the ionic strength [43].

3.3. Thermal properties of the composite fibers

DSC experiments with fiber mats prepared from soy protein and lignin are shown in Fig. 4 and Table 3. Two endothermic transitions were observed for each protein fiber mat, one weak peak around 95 °C and a broader one around 120 °C. Two thermal transitions have been reported in DSC analyses of soy proteins, assigned to the denaturation of the main globulins present in soy isolate, β-conglycinin (76 °C) and glycycin (91.5 °C) [44]. The higher transition temperatures obtained in this study (95 °C and 120 °C) were obtained in the second heating cycle (i.e. after removing the thermal history), direct comparison is not possible with the aforementioned values, but it is important to consider other factors such as moisture content, the source of the protein and the method of purification might.
have an influence. For instance, water acts as a plasticizer for the proteins; therefore after removal of moisture, an increase in thermal transition temperature is expected. DSC evaluation of the fiber mats also exhibited two transition temperatures, the smallest one around 95°C and the highest thermal transition shifted towards the Tg of lignin (130°C) as the concentration of lignin increased (for both fibers types, based either on glycinin or isolate). These results suggest that the thermal stability of the fiber mats increased with the addition of lignin. Similar results were observed in the evaluation of soy protein plastics with alkali lignin as a filler, resulting in plastics with improved mechanical and thermal properties; such effect was attributed to strong interactions between lignin and soy proteins [37].

In the present case, the interactions between lignin and soy protein can be also benefit from the presence of PEO in the mixture as has been reported previously for systems containing soy protein and PEO [18,19]. It has been also pointed out that PEO interacts favorably with proteins through hydrogen bonding, via coordination contacts of positively charged amino acid residues, and by hydrophobic interactions [33]. Similarly, lignin contains phenolic and aliphatic hydroxyl groups that can interact with PEO, which will affect the thermal behavior of the fiber mats. No evidence of a melting peak of PEO was observed in the DSC curves; this suggest that PEO interacts favorably with lignin and the soy proteins producing a miscible blend. Similar results have been obtained for fibers from soy isolate and PEO blends – the lack of melting peak was attributed to good miscibility of the polymers [19].

The results in Fig. 4 also indicate better miscibility of lignin with glycinin as evidenced by the disappearance of the glycinin peak, around 120°C. This supports the SEM observations of apparent aggregates in isolate-containing samples (I2, I3, I4) but not in samples containing glycinin. The immiscibility of kraft lignin–SPI mixtures has been reported in the evaluation of sheets [37] formed from solutions of these biopolymers with a high concentration of lignin. It was pointed out that such immiscibility improved the mobility of protein molecules in the mixture [37]. The increase in the values of ΔCp shown in Table 3 suggest an enhancement of molecular mobility of protein in lignin as the concentration of lignin increases.

3.4. FT-IR analysis

FT-IR measurements were carried out to evaluate the interactions between soy proteins and lignin in the electrospun fiber
The peaks at 1600, 1540, 1505–1510 cm\(^{-1}\) isolate indicate two regions of interest: from 3800 to 2750 cm\(^{-1}\) crystalline phase [45]. The intensity, shape, and position of this triplet for PEO depends on the crystallinity of the polymer and the fingerprint region from 1700 to 750 cm\(^{-1}\) are indicated by the arrows.

Transition temperatures for composite fiber mats.

Results shown in Fig. 5 for samples from both glycinin and isolate indicate two regions of interest: from 3800 to 2750 cm\(^{-1}\) and the fingerprint region from 1700 to 750 cm\(^{-1}\). The broad band observed around 3400 cm\(^{-1}\) is characteristic of hydroxyl groups and the small peak around 2900 cm\(^{-1}\) corresponds to CH stretching. It can be observed that for fiber mats from both protein samples the peak around 3400 cm\(^{-1}\) broadens as the concentration of lignin increases, which suggests improved interactions between soy proteins and lignin through hydrogen bonding, enhanced by the presence of PEO. A closer look to the region 1800–800 cm\(^{-1}\) can be observed in Fig. 5. In this region each component displays different fingerprints: for instance PEO displays a triplet (1152, 1100, 1069) with a maximum at 1100 cm\(^{-1}\) which has been attributed to its crystallinity phase [45]. The intensity, shape, and position of this triplet for PEO depends on the crystallinity of the polymer and interactions of C–O–C groups with other groups in the blend [19,45]. This peak was absent in FT-IR spectra of the fiber mats, which suggest favorable interactions between the PEO, soy protein, and lignin in the mixture. Similar results have been observed for pure blends of SPI with PEO, indicating the reduction or disappearance of crystallinity for the PEO in the blends [19]. The characteristic peak for lignin in this region can also be observed in Fig. 5. The peaks at 1600, 1540, 1505–1510 cm\(^{-1}\) correspond to aromatic skeletal vibrations, the peak at 1460 cm\(^{-1}\) correspond to aromatic skeletal vibrations combined with C–H in plane deformation; the peak at 1366 corresponds to phenolic OH groups and aliphatic C–H stretch; the peak at 1266 is assigned to C–O stretch and aromatic skeletal vibration of guaiacyl ring. Finally, the peaks at 1214, 1134, 1076 and 1044 cm\(^{-1}\) correspond to aromatic in plane C–H deformation. It can be observed that the lignin peaks in the region from 1271 to 1000 cm\(^{-1}\) develop in the fiber mats samples and that the strength of these peaks increased with the concentration of lignin in the sample (i.e., from sample 1 to 4). Similarly the weak peak corresponding to OH phenolic group was observed in the fiber samples.

Regarding the fingerprint of the protein, the peaks characteristic of the amide bands correspond to the amide bonds linking the amino acid chains, in the 1800–800 cm\(^{-1}\) region. The amide I band (1600–1690 cm\(^{-1}\)) corresponds to stretching vibrations of the C=O bond of the amide, the amide II region (1480–1575 cm\(^{-1}\)) corresponds to bending of the N–H bond, whereas the amide III band (1400–1200 cm\(^{-1}\)) generally contains information on the secondary structure or coiling of the peptide sequence [46,47]. The amide I band can provide insights about the secondary structure of the protein by appropriate deconvolution of the peaks. In the case of glycinin these three amide bands appear at 1645 cm\(^{-1}\) (amide I), peaks at 1545 cm\(^{-1}\) (amide II), and 1240 cm\(^{-1}\). The corresponding peaks of these amide bands are very weak in the samples containing lignin and soy protein. For fibers containing glycinin–lignin, the amide band only appears for sample G1. The amide II band is only present as a weak peak in sample G1. Similarly the amide I band is observed with similar shape in sample G1 but as a weak peak for samples G2, G3, and G4: however this weak peak shifts toward higher wavenumbers (1664 cm\(^{-1}\)). Similar observations apply for fibers containing soy protein isolate: the amide III band disappears in FT-IR spectra of all SPI samples. The amide II band is observed as a weak peak only in spectrum of sample I1. The amide I peak in sample I1 displays a similar shape than that for pure soy isolate but as was the case of glycinin, it shifts toward higher wavenumbers (1664 cm\(^{-1}\)) for samples I2, I3 and I4. The weak peak observed for amide I region in fibers of both glycinin and SPI with increasing amount of lignin indicates the loss of secondary structure of the protein in these mixtures. This denaturation (unfolding) of the protein molecule improves entanglement with the lignin and PEO molecules in the blend, which in turn is favorable to achieve uniform fiber formation by electrospinning. The disappearance of the amide II and III band with increasing concentration of lignin might be an indication of good miscibility of these two biopolymers.

Altogether, the results indicate the compatibility between soy proteins and lignin, two underutilized materials readily available as byproducts from different processes and that are suitable for the production of added value materials for different applications.

3.5. Wettability of lignin–soy protein electrospun fibers

The wettability of the composite electrospun fibers mats can be assessed from the contact angle data included in Fig. 6. A reduction in the initial advancing contact angle is observed as the lignin content in the fibers increases, i.e., the fibers become more hydrophilic. This increase in hydrophilicity can be because of the

<table>
<thead>
<tr>
<th>Sample</th>
<th>G1</th>
<th>G2</th>
<th>G3</th>
<th>G4</th>
<th>I1</th>
<th>I2</th>
<th>I3</th>
<th>I4</th>
<th>PEO</th>
<th>Glycinin</th>
<th>SPI</th>
<th>Lignin</th>
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<tr>
<td>Tg, (°C)</td>
<td>93.8</td>
<td>95.3</td>
<td>95.1</td>
<td>94.8</td>
<td>95.1</td>
<td>95.5</td>
<td>94.2</td>
<td>95.4</td>
<td>68.7*</td>
<td>94.2</td>
<td>94.5</td>
<td>130</td>
</tr>
<tr>
<td>Tg2, (°C)</td>
<td>129.8</td>
<td>132.4</td>
<td>133.5</td>
<td>132</td>
<td>125.6</td>
<td>125</td>
<td>133.1</td>
<td>134</td>
<td>–</td>
<td>120.3</td>
<td>124.7</td>
<td>–</td>
</tr>
<tr>
<td>ΔH (J/g)</td>
<td>2.17</td>
<td>3.98</td>
<td>5.37</td>
<td>6.03</td>
<td>2.45</td>
<td>3.83</td>
<td>3.81</td>
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<td>20.9</td>
</tr>
<tr>
<td>ΔCp at Tg</td>
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<td>0.08</td>
<td>0.11</td>
<td>0.12</td>
<td>0.049</td>
<td>0.077</td>
<td>0.076</td>
<td>0.090</td>
<td>–</td>
<td>0.04</td>
<td>0.03</td>
<td>0.42</td>
</tr>
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</table>

* Melting temperature for PEO.
nature of the kraft lignin used (for instance it is more hydrophilic compared to an organosolv lignin). No changes in contact angle were observed within short times (<30 s) but thereafter the components of the fiber mats started to dissolve into the water droplets. The results shown in Fig. 6 also suggest that phase separation might be occurring when the fibers form in the electrospinning process; as a result the outer layer of the fibers is enriched by the component that is in higher proportion in the polymer blend. The samples containing large amount of protein (protein content of 78%) have a higher initial contact angle. This can possibly be due to the denaturation of the protein in solution upon exposure of the hydrophobic amino acids to the surface. One can speculate that such denaturation effect is further enhanced by the high electric field present during electrospinning. The changes in contact angle can also be ascribed to the roughness of the fiber mat. Compared to samples with high lignin content, the fibers rich in protein typically displayed a smaller diameter and provided a less porous structure (Fig. 2), which affected the interactions with water. This hydrophilic behavior of the fiber mats could be changed by crosslinking.

4. Conclusions

Sub-micron fibers from soy protein isolate and glycinin mixed with lignin and PEO coadjuvant were successfully produced. An increase in fiber diameter was observed with successive lignin loading and favorable interactions between glycinin and lignin were evidenced by the disappearance of glycinin DSC transition peak as the lignin content increased. An increased thermal stability was observed by a small increase in thermal transition compared to the Tg of lignin (130 °C). The interactions between soy proteins and lignin are favored by increasing hydrogen bonding, which is further improved by the presence of PEO in the mixture. Overall lignin and soy proteins can be used to produce new fiber materials suitable for applications that can take advantage of the functional groups present in both lignin and soy proteins.

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