

Antimicrobial and Ultraviolet Protective Properties of Nanocomposite Fiber Webs

G. S. SivaKumar

Garment textile technology, SSM Polytechnic College

Abstract - Lignin/poly (vinyl alcohol) (PVA) nano composite fibers with different lignin concentrations were developed via electro spinning to investigate further possible applications of lignin, an under-utilized renewable biomass material. The antimicrobial and ultraviolet (UV) absorption properties of lignin/PVA nano composite fibers were evaluated to determine whether the inherent functionalities of lignin remain in the final material. An environmentally benign cross-linking method was sought to increase the stability of lignin/PVA nano composite fibers in aqueous media. The cross linking and in solubilization of the lignin/PVA nano composite fibers was achieved by combining several cross linking techniques: water vapor treatment at 80_C for 180 min, photo-irradiation for 30 min under visible light at a distance of 17 cm, and heat treatment at 200_C for 60 min. Both lignin/PVA nano composite fiber webs—containing 50 and 85 wt% of lignin at a 3.0 g/m² web area density, respectively—showed a 99.9% reduction rate against *Staphylococcus aureus*, but no reduction against *Escherichia coli*. The same systems exhibited ultraviolet protection factors (UPF) of >50, indicating excellent UV protection. These findings demonstrate the potential of lignin-based composite fibers and may widen the range of applications for this biomass material.

Index Terms - lignin, nano composite fiber, antimicrobial property, ultraviolet protection, electro spinning, cross linking.

INTRODUCTION

Environmental concerns and the depletion of fossil fuels have motivated the fiber industry to investigate the potential of biomass as an alternative to petroleum resources. Biopolymers, such as polysaccharides and animal protein-based polymers, are well-known examples of biomass-based polymeric materials. Biopolymers are renewable, biodegradable, and biocompatible, as well as cheap and widely available.¹ In addition, some of them exhibit intrinsic antibiotic,² antioxidant,³ and ultraviolet (UV)-protective

properties,^{4,5} which are useful from a fiber-application perspective. Therefore, biopolymer-based fibers are perceived not only as alternatives to petroleum-based synthetic fibers, but also as new fiber materials for value-added functional products.

Lignin is a polyphenolic polymer found in the cell walls of ligno cellulosic biomass, and one of the most abundant natural polymers in the biosphere. Although forest-using industries generate ~50 million tons of lignin annually, the material is under-utilized as a fuel as it is perceived to be waste.¹ However, the recent interest in and demand for new biopolymers have led to research on the characterization of lignin, which has been found to be inherently antimicrobial,⁶ anti-oxidizing,^{6,7} and UV-protective.^{4,5} Dong et al.⁶ examined the antimicrobial and antioxidant properties of various lignin extracts and of commercially available lignin. Strong antioxidant properties were found in all types of lignin. However, the antimicrobial properties were selective, in that they showed antimicrobial effectiveness against yeast and Gram-positive bacteria, such as *Listeria monocytogenes* and *Staphylococcus aureus*, but not against Gram-negative ones, such as *Escherichia coli* and *Salmonella enteritidis*. Qian et al.⁵ reported a significant enhancement in the UV absorption properties when 2–10wt% of lignin was added to commercial sunscreen agents. Although various intrinsic properties of lignin have been investigated, relatively

little research has been conducted on lignin-based processed composites. Hence, the use of lignin as a polymer additive remains limited to the food, cosmetic, and pharmaceutical industries despite its strong potential for high-value applications in more diverse fields, including functional fibers and textiles. Recently, efforts have been made to develop lignin based polymer composites, such as films,⁸ fibers,⁹ and hydrogels.¹⁰ One of these attempts involved

transforming lignin into nano fibers by electro spinning, a technique for fabricating continuous polymeric ultrafine fibers. Dall Meyer et al.⁹ and Ago et al.¹¹ successfully electro spun lignin-based nano composite fibers by blending lignin with poly (ethylene oxide) (PEO) and with poly (vinyl alcohol) (PVA), respectively. The main challenge in the electro spinning of lignin is its low visco elasticity due to its low molecular weight.

The electro spinnability of lignin was significantly enhanced by the use of easily electro spun synthetic polymers.^{9,11,12} However, as Dall Meyer et al.⁹ and Schreiber et al.¹² fabricated lignin-based nano composite fibers to produce precursors for carbon fibers, they focused on ways to control the diameters and morphology of the resulting fibers in order to yield high quality carbon fibers. In other words, there has been a scarcity of research on the functionalities of lignin based nano composite fibers for use as final products. Fibers made of water-soluble polymers, such as alkali lignin with low sulfonate content and PVA, must be treated to increase their stability in the presence of water before they can be used in certain applications. To make polymer materials insoluble in aqueous media, physical or chemical modifications are applied to increase the content of the crystalline regions or the degree of cross linking. Although chemical cross-linking methods using chemicals such as formaldehyde or glutaraldehyde have been reported,^{13,14} more eco-friendly approaches are preferred for environmental reasons. Physical cross-linking methods, such as heat treatment^{15,16} and photo-crosslinking,^{17,18} have been reported to be effective for the cross linking and in solubilization of nanofibers made of various water-soluble polymers without using toxic chemicals. Several physical and chemical cross-linking methods for lignin and PVA have been reported.^{13–15} However, to date, there have been no reports of chemical or physical cross-linking methods for lignin/PVA nano composite fibers. Thus, an effective and environmentally benign cross linking method for these fibers needs to be examined to be able to further broaden their applications.

A proper investigation of the cross-linking methods for lignin-based composite fibers and their functionalities would extend the use of polymers from renewable resources and widen the range of applications for this biomass material. This research

would be useful for industries working on designing future value-added composite products based on lignin. In this study, lignin/PVA nanocomposite fibers were fabricated by electrospinning, and an environmentally benign crosslinking method for the resulting fibers was developed by combining several physical crosslinking techniques without using toxic chemicals. The morphological properties and changes in the crystallinity of the lignin/PVA nanocomposite fibers were examined before and after the crosslinking treatment. The antimicrobial and UV-protective properties of the lignin/PVA nanocomposite fibers were evaluated to determine whether the inherent functionalities of lignin remained after the electrospinning process.

MATERIALS AND METHODS

Materials

Water-soluble lignin was selected to avoid the use of an organic solvent. Alkali lignin with low sulfonate content ($M_w \approx 10,000$, Sigma Aldrich Co., USA) was used as received, and PVA (>99% hydrolyzed, $M_w \approx 89,000-98,000$, Sigma Aldrich Co., USA) was used to facilitate the fiber formation of lignin. Distilled water was used as the solvent.

Preparation of spinning solutions

To prepare the electrospinning solution, PVA powder was dissolved in distilled water, and lignin was then added to the PVA precursor solution. The lignin/PVA solution was stirred at 80°C for 6 h. In a previous study by our research group,¹⁹ 11 lignin/PVA hybrid solutions were prepared with different lignin/PVA mass ratios, and lignin/PVA nanocomposite fibers were then electro spun under various spinning conditions, including various feed rates, needle gauges, electric voltages, and tip-to-collector distances, to find the optimal concentration and spinning conditions. The electro spinnability and morphology of the resulting fibers were examined, and bead-free uniform lignin-based nanocomposite fibers were obtained. Here, two spinning solutions with different lignin/PVA mass ratios were selected based on our previous study¹⁹ to further investigate the functionalities of lignin/PVA nanocomposite fibers. The two solutions were prepared as follows: (a) an 8wt% PVA precursor solution and a 1:1 lignin/PVA mass ratio; and (b) a

5wt% PVA precursor solution and a 5.6:1 lignin/PVA mass ratio. The lignin concentrations of the resulting bicomponent fibers were 50 and 85 wt%, respectively. An 11wt% PVA solution was prepared to fabricate pristine PVA nanofibers as a control. The prepared solutions were kept at room temperature for 24 h before being electro spun.

Electrospinning process

A vertical electrospinning set-up with a two-axis robot system (NNC-ESP200R2, NanoNC, Korea) was used. The solutions were electro spun on a substrate material (polyester nonwoven) under the optimal spinning conditions determined in our previous study,¹⁹ that is, a voltage of 25 kV, a working distance of 15 cm, and a feed rate of 0.4 ml/h through a 25-gauge needle (0.25mm i.d.) The resulting fibers were dried at 50_C in a vacuum oven (OV-11/12, Jeio Tech, Korea) for 24 h to remove any residual water.

Fiber morphology

The morphology of the electro spun lignin/PVA nanocomposite fibers was examined using a field-emission scanning electron microscope (FE-SEM) (JSM 6701-F, JEOL Ltd, Japan) equipped with an energy dispersive Xray (EDX) analysis system after sputter-coating with Pt/ Pd. The chemical composition of the lignin/PVA nanocomposite fibers was determined by EDX analysis. PVA, were attempted by combining two physical crosslinking techniques. Photo-crosslinking and heat treatment were selected based on previous research,^{15–18} and further water vapor treatment²⁰ was applied to the process to enhance the photo-crosslinking efficacy. Three experimental routes were used to crosslink the lignin/PVA nanocomposite fiber samples (Figure 1): (1) heat treatment at 200_C for 60 min; (2) photo-irradiation prior to the heat

Crosslinking treatment

Crosslinking and in solubilization of the lignin/PVA nanocomposite fibers fabricated from the water-soluble polymers, that is, alkali lignin with low sulfonate content and treatment; and (3) water vapor treatment prior to the photo-irradiation and heat treatment to enhance the crosslinking efficiency. The experimental conditions of the photo-crosslinking and water vapor treatment were altered to find suitable ones for the crosslinking treatment. Photo

crosslinking was implemented with visible (420 nm) and UVC (253.7 nm) light at a distance of 17 cm for 30 min, and the water vapor treatment was conducted at 80_C for 30, 60, and 180 min. To investigate whether the crosslinking treatment had stabilized the lignin/PVA nanocomposite fibers against dissolution in water, composite fiber webs treated by the three different experimental routes were immersed in water at 18_C for 1 h before being oven dried.

The fiber morphology was then examined using FE-SEM. In addition, the lignin/PVA nanocomposite fibers were characterized by X-ray diffraction (XRD) (Ultima IV, RIGAKU, Japan) to investigate the crystallinity before and after the crosslinking treatment. The presence of lignin in the nanofiber web was confirmed by locating sulfone with EDX spectroscopy after the crosslinking treatment.

Antimicrobial properties

The antimicrobial properties of the lignin/PVA nanocomposite fibers were examined quantitatively in accordance with ASTM E 2149-10 (Standard Test Method for Determining the Antimicrobial Activity of Immobilized Antimicrobial Agents under Dynamic Contact Conditions). Two representative microorganisms, *Staphylococcus aureus* (ATCC 6538, Gram positive bacterium) and *Escherichia coli* (ATCC 25922, Gram-negative bacterium), were used for the assessment. Specimens were prepared with a web area density of 3.0 g/m², and the crosslinking treatment was applied before the antimicrobial evaluation. The specimens were immersed in an inoculated buffer solution within a flask

and were agitated with a shaker. The reduction in the test organisms after a 1 h contact time with each specimen was then calculated by equation (1) $R \% = \frac{A - B}{A} \times 100$ where R is the reduction rate of the number of colonies, A is the number of bacterial colonies in the flask containing the test specimen after a specified contact time, and B is the number of initial bacterial colonies in the flask.

UV transmission properties

The transmission of UV rays through the lignin/PVA nanocomposite fiber webs was measured in accordance with the American Association of Textile Chemists and Colorists (AATCC) Test Method 183-2004 (Transmittance or Blocking of Erythemally

Weighted Ultraviolet Radiation through Fabrics). The UV transmission data were collected using an ultraviolet-visible near infrared (UV-Vis-NIR) spectrophotometer (Perkin-Elmer Lambda 950, PerkinElmer, USA) in the 280–400nm wavelength range at intervals of 2 nm. Lignin/PVA nanocomposite fiber webs were prepared with a web area density of 3.0 g/m², and the transmission was measured three times for each sample. The results are the mean values of these measurements. The UV transmission data were used to calculate the ultraviolet protection factor (UPF), which indicates the degree to which a material reduces the UV exposure.

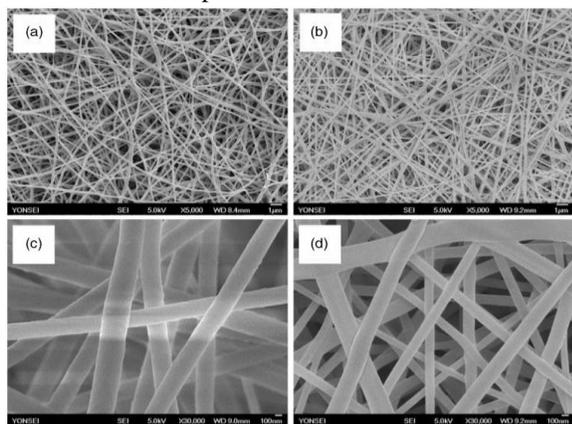


Figure 2. Scanning electron microscope images of as-spun lignin/poly(vinyl alcohol) nanocomposite fibers with different lignin concentrations: (a) 85% ($\times 5000$); (b) 50% ($\times 5000$); (c) 85% ($\times 30,000$); (d) 50% ($\times 30,000$).

where E_{λ} is the relative erythemal spectral effectiveness, S_{λ} is the solar spectral irradiance (W/cm²/nm), T_{λ} is the mean measured transmittance of the specimen (%), and $\Delta\lambda$ is the measured wavelength interval (nm).

RESULTS AND DISCUSSION

Fiber morphology

Lignin/PVA nanocomposite fibers with lignin concentrations of 50 and 85wt% were successfully fabricated by electrospinning. Two lignin/PVA polymer solutions were electrospun based on the spinning conditions used in our previous study,¹⁹ which were applicable to the fabrication of lignin/PVA nanocomposite fibers with 85wt% lignin concentration. As a result, lignin/PVA nanocomposite fibers with 85wt% lignin concentration were obtained

with a voltage of 25 kV at a working distance of 15 cm and a feed rate of 0.4 ml/h through a 25-gauge needle, as shown in Figure 2(a). However, the working distance was modified from 15 to 10 cm in order to electro spin the lignin/PVA polymer solution with less lignin content owing to its lower viscosity. A scanning electron microscope (SEM) image of the lignin/PVA nanocomposite fibers with 50wt% lignin concentration is provided in Figure 2(b). The modified conditions yielded fine continuous fibers with diameters

Figure 2. of 95–230nm (Figure 2(d)), that is, thinner than those

with a higher lignin content (265–375 nm) (Figure 2(c)).

Crosslinking of lignin/PVA nanocomposite fibers

Water-soluble biopolymers can be prepared by environmentally friendly manufacturing processes, but a post-treatment is needed to prevent humidity-induced structural changes for practical applications. Since, to our knowledge, crosslinking methods for lignin/PVA nanocomposite fibers have not yet been reported, this study combined several physical treatments, including photo-crosslinking and heat treatment, to develop an environmentally benign crosslinking method that does not use toxic chemicals. The PVA (C₂H₄O)_n and lignin (CH₂O-H₂O₃S-2Na-Unspecified) used in this study have numerous hydroxyl groups, which are possible reaction sites for hydrogen bonding. This affects the water affinity and solubility of the fabricated nanocomposite fibers because dissolving in water happens with the generation of hydrogen bonding between the polymer and water.²¹ Thus, in this study, inducing inter- and intramolecular crosslinking prior to the formation of the hydrogen bonding was proposed to develop a method for reducing the affinity of the fibers with water.

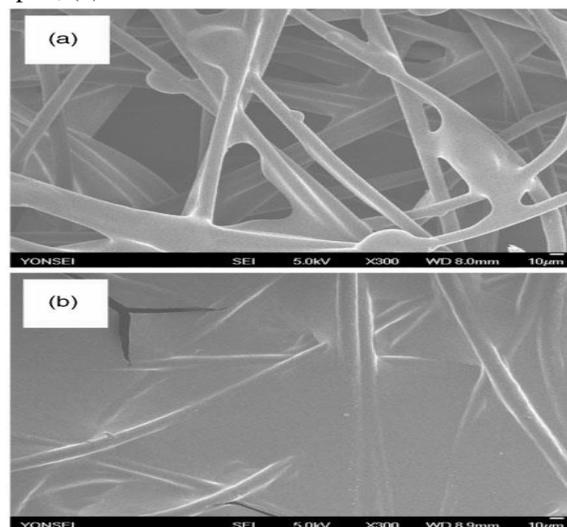
The nanocomposite fiber samples were first heat treated at 200°C for 60 min, as shown in Figure 1.

This heat treatment condition was determined by preliminary experiments and involved a temperature below the thermal degradation temperature of lignin and PVA used in this study. For reference, PVA nanofibers and lignin used in this study began to decompose at ca. 230°C and ca. 246°C, respectively. According to Wong et al.,¹⁵ applying heat treatment at 135°C for 60 min successfully stabilized pure PVA

nanofibers from disintegrating in water. It was reported that heat treatment induced the formation of small crystallites and the crystallite domains served as physical crosslinks to hold the structure together.^{15,22} In this study, however, the surface of the heat-treated-only sample became film-like when exposed to water at 18_C for 1 h, as shown in Figure 3(b). On the other hand, the as-spun samples without heat treatment completely disintegrated when immersed in water, leaving the nonwoven substrate material only, as shown in Figure 3(a). This implies that a certain amount of physical crosslinking developed under heat treatment. However, the presence of lignin in the nanocomposite fibers may require stronger crosslinking treatment to insolubilize all constituents. Photo-crosslinking was used to obtain further crosslinking and, thus, to enhance water resistance. Photo-crosslinking is usually achieved with the aid of photo-initiators or crosslinkers, which generate free radicals by self-photolysis and subsequently initiate crosslinking. Although crosslinking generally occurs in the presence of crosslinking agents, the problem is that most photo-initiators and crosslinkers are toxic chemicals. However, according to research on the effects of UV irradiation on photosensitive polymers,^{18,23} UV crosslinking occurs without such crosslinkers if the given polymer generates free radicals by chain scission resulting from UV radiation (UVR) exposure. Lignin has UV-absorbing properties accompanying free-radical formation caused by photo-oxidation and a subsequent chain scission reaction of its chromophoric functional groups, such as phenolic ones.^{24,25} Thus, photo crosslinking was attempted without chemical crosslinkers and the probable crosslinking effect of radicals formed by the photolysis of lignin was investigated. Photo-crosslinking was conducted under visible (420 nm) and UVC (253.7 nm) light, and with two other fixed parameters: a 17-cm distance between the light source and the samples; and a 30-min duration. The fixed parameters were determined by preliminary experiments, a narrower distance or longer treatment time resulted in the sample being damaged by excessive irradiation. Figures 4(a) and (b) show the SEM images

Figure 3. Scanning electron microscope images of electro spun lignin/poly (vinyl alcohol)

nanocomposite fibers after immersion in water: (a) as spun; (b) heat-treated.



Comparing the fiber morphologies of further photo irradiated samples of lignin/PVA nanocomposite fibers after immersion in water for UVC and visible light, respectively. Fibrous structures were more persistent in the samples treated additionally with visible light (Figure 4(b)) than in those treated with heat alone (Figure 3(b)). However, the UVC-irradiated samples (Figure 4(a)) dissolved and lost their fibrous structure in the same way as the heated-only ones (Figure 3(b)). This shows that photo-crosslinking with heat treatment makes the samples more water-resistant; using visible light at a distance of 17 cm for 30 min worked best for this purpose. In summary, consecutive reactions of photo-oxidation, chain scission, and crosslinking of lignin and PVA resulted from the combined treatment of photo-crosslinking and heat treatment are proposed as a possible mechanism of inducing the crosslinking of lignin/PVA nanocomposite fibers, but further study is needed for an exact explanation. Unfortunately, in solubilization was not sufficiently implemented. According to Lignon et al.,²⁰ the presence of oxygen (which consumes free radicals) was pointed out as a factor inhibiting the crosslinking reaction. Related to this problem, Nhi²⁶ suggested the solution of surrounding the samples with water vapor (thereby creating conditions similar to those of an inert atmosphere); water vapor acts as an inert gas, and thus, reduces oxidation. The aforementioned approach was adopted, and water vapor treatment was added prior to photo-

crosslinking. The duration of this additional treatment was set to 30, 60, and 180 min to investigate the effect of the amount of water vapor attached to the sample surface on photo-crosslinking efficacy and, hence, on the degree of insolubilization. The results are shown in Figure 5 as SEM images of lignin/PVA nanocomposite fiber samples after immersion in water. The samples were treated with water vapor for different durations but the same conditions for photo-crosslinking and heat treatment.

The physical integrity of the fibrous web was better with water vapor treatment than without it. The degree of sample dissolution decreased with longer exposure to water vapor, with the most-persistent fibrous and pore structures being those in the 180-min samples. The same samples were stable with regard to their degree of shrinkage after immersion and drying, which indicates that the method resulted in stable macro- and micro morphologies. Hence, water vapor treatment at 80_C for 180 min, photo-irradiation for 30 min under visible (420 nm) light at a distance of 17 cm, and heat treatment at 200_C for 60 min was selected as the best one achieved among the parameters tested for crosslinking and insolubilizing lignin/PVA nanocomposite fibers. Our results demonstrated that the crosslinking method determined was effective in stabilizing lignin/

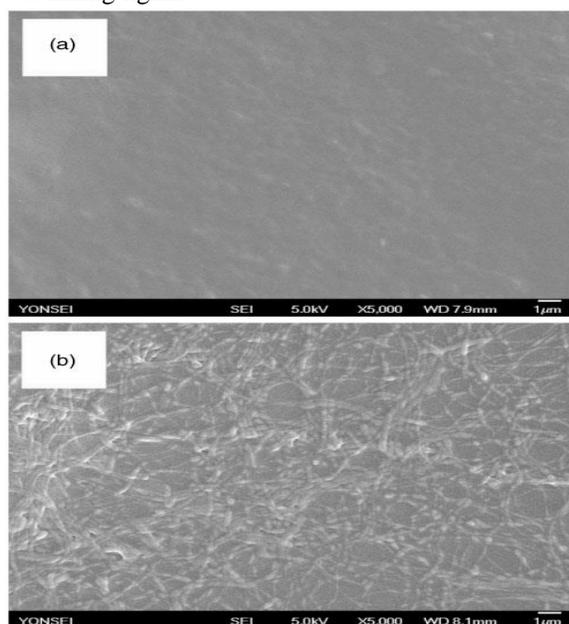


Figure 4. Scanning electron microscope images of electro spun lignin/poly (vinyl alcohol) nanocomposite fibers with further photo-irradiation

treatment after immersion in water: (a) irradiated under ultraviolet C; (b) irradiated under visible light. PVA nanocomposite fibers against dissolution in water by means of physical crosslinking techniques and the unique features of lignin polymers, without the use of toxic chemicals. XRD characterization was used to observe the changes in crystallinity of lignin/PVA nanocomposite fibers before and after crosslinking. As shown in Figure 6, the XRD spectrum of the untreated fibers revealed a very weak and broad peak at $2\theta/421-22.2^\circ$, indicating the amorphous state of the specimen. After crosslinking, however, two new peaks appeared at $2\theta/420^\circ$ and 31.5° , which are attributable to diffraction by the PVA crystalline structure. This indicates that the crystallinity of the nanocomposite fibers increased after the crosslinking treatments. Also, EDX analysis was conducted to determine if lignin was retained in the nanocomposite fibers after electrospinning and crosslinking. The presence of lignin was confirmed by locating sulfone with EDX spectroscopy. Table 1 summarizes the EDX analysis results of lignin/PVA nanocomposite fibers and pristine

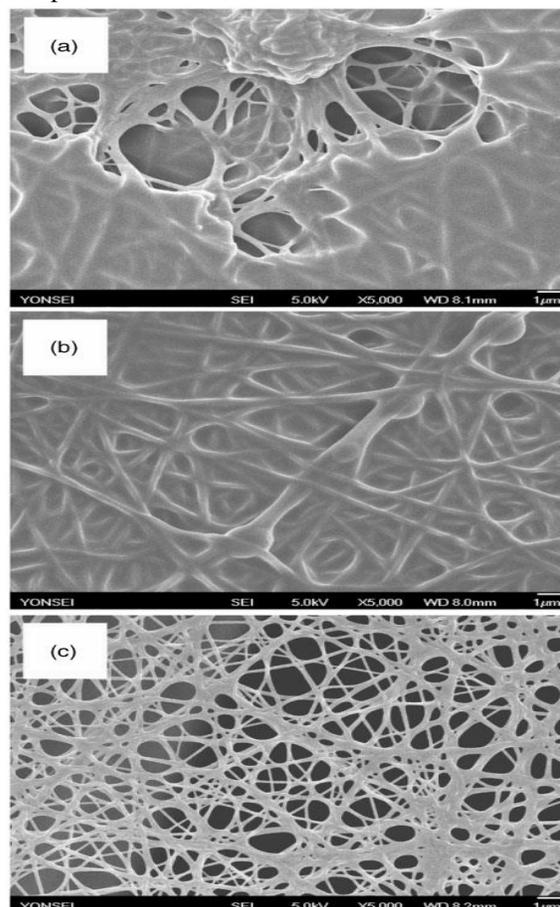


Figure 5. Scanning electron microscope images of electro spun lignin/poly (vinyl alcohol) nanocomposite fibers with different water vapor treatment time prior to photo-irradiation and heat treatment: (a) 30 min; (b) 60 min; (c) 180 min. (The images were taken after immersion in water.)

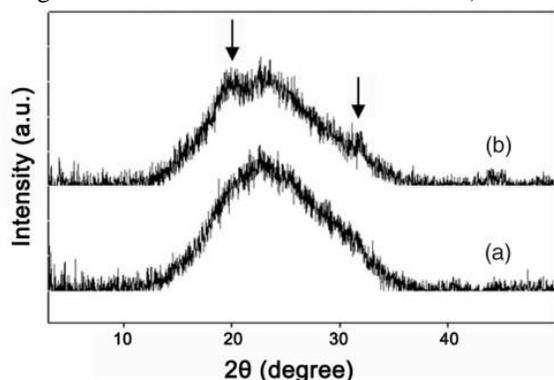


Figure 6. X-ray diffraction spectra of electrospun lignin/ poly (vinyl alcohol) nanocomposite fibers: (a) before crosslinking; (b) after crosslinking

Antimicrobial properties of lignin/PVA nanocomposite fibers

The antimicrobial properties of lignin/PVA nanocomposite fibers were investigated to examine if they are retained after lignin is transformed into nanofibers. These properties were assessed for both pristine and lignin-containing (50 and 85 wt%) PVA nanofibers to examine the effect of lignin content on the antimicrobial activity of lignin/PVA nanocomposite fibers. Two microorganisms were used for the assessment: *Staphylococcus aureus* as a representative Gram-positive bacterium and *Escherichia coli* as a representative Gram-negative one. The antimicrobial activities of lignin/PVA nanocomposite fibers are presented in Table 2 as percentages of bacterial reduction. Both the 50 and 85wt% lignin/ PVA nanocomposite fibers (L50 and L85, respectively, in Table 2) exhibited 99.9% reduction of *Staphylococcus aureus* (Gram-positive bacterium). Our findings clearly show that the UV-protective properties of nanocomposite fibers can be significantly improved with the incorporation of 50wt% lignin. This indicates that, as in the antimicrobial case, lignin plays a significant role as a functional agent in UV protection.

CONCLUSIONS

Lignin, the second most abundant natural polymer next to cellulose, is being viewed afresh as a renewable resource and efforts are being made to develop more valuable applications of under-utilized lignin. This study aimed to develop lignin-based nanocomposite fibers and evaluate if the inherent functionalities of lignin, such as its antimicrobial and UV absorption properties, were retained after being transformed into nanofibers, with a view to investigating further applications of lignin. Lignin/PVA nanocomposite fibers with different lignin concentrations were fabricated via electrospinning, and the antimicrobial and UV absorption properties were examined. Since lignin/PVA nanocomposite fibers made from water-soluble polymers require crosslinking for practical applications, an environmentally benign crosslinking method was developed by combining several physical crosslinking techniques. The best conditions achieved among the parameters tested for crosslinking and insolubilizing lignin/PVA nanocomposite fibers were water vapor treatment at

80_C for 180 min, photo-irradiation for 30 min under visible light at a distance of 17 cm, and heat treatment at 200_C for 60 min. XRD characterization and SEM images before and after the crosslinking treatment indicated that the crosslinking conditions were effective in stabilizing the lignin/PVA nanocomposite fibers against dissolution in water. For the antimicrobial evaluation,

lignin-based nanocomposite fibers provided strong antimicrobial effects against *Staphylococcus aureus*, a representative Gram-positive bacterium, but not against *Escherichia coli*, a representative Gram-negative bacterium. Our results agreed with those of previous research that evaluated the antimicrobial activity of lignosulfonate, the type of lignin used in this study. The incorporation of 50% lignin in nanocomposite fibers significantly reduced the transmission of UVR, giving UPFs of >50, which indicates excellent UV protection. Our findings demonstrate the potential of lignin/ PVA nanocomposite fibers as not only eco-friendly materials but also advanced functional ones. These results may unlock the potential of lignin as an under-utilized renewable biomass material and widen the range of its application.

REFERENCES

- [1] Thakur VK, Thakur MK, Raghavan P, et al. Progress in green polymer composites from lignin for multifunctional applications: a review. *ACS Sustainable Chem Eng* 2014; 2:1072–1092.
- [2] Cowan MM. Plant products as antimicrobial agents. *Clin Microbiol Rev* 1999; 12: 564–582.
- [3] Cazacu G, Capraru M and Popa VI. Advances concerning lignin utilization in new materials. In: Thomas S, Visakh PM and Mathew AP (eds) *Advances in natural polymers*. Dordrecht: Springer, 2013, pp.255–312.
- [4] Toh K, Nakano S, Yokoyama H, et al. Anti-deterioration effect of lignin as an ultraviolet absorbent in polypropylene and polyethylene. *Polym J (Tokyo, Japan)* 2005; 37: 633.
- [5] Qian Y, Qiu X and Zhu S. Lignin: a nature-inspired sun blocker for broad-spectrum sunscreens. *Green Chem* 2015; 17: 320–324.
- [6] Dong X, Dong M, Lu Y, et al. Antimicrobial and antioxidant activities of lignin from residue of corn stover to
- [7] ethanol production. *Ind Crops Prod* 2011; 34: 1629–1634.
- [8] Dizhbite T, Telysheva G, Jurkjane V, et al. Characterization of the radical scavenging activity of lignins—natural antioxidants. *Bioresour Technol* 2004; 95: 309–317.
- [9] Li XF. Preparation and properties of biodegradable sodium lignosulfonate/poly (vinyl alcohol) blend films.