ELECTROSPUN LIGNIN NANOFIBERS

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ABSTRACT: *Lignin-based nanofibers present significant potential for use in technical applications as a sustainable alternative to conventional materials. In this study, the electrospinning of lignin nanofibers was investigated. Polyacrylonitrile (PAN) and polyvinyl alcohol (PVA) were selected as carrier polymers to facilitate the electrospinning process. Lignin/polymer solutions with varying mixing ratios were electrospun under different applied voltages. The morphology of the resulting nanofibers was characterized using scanning electron microscopy (SEM). The results demonstrated the successful production of bead-free lignin nanofibers using both carrier polymers. Notably, the finest nanofibers were obtained with PAN, whereas the use of PVA enabled the incorporation of a higher lignin content (>80%) within bead-free nanofibers.*

Keywords: *Electrospinning, nanofiber, lignin, carrier polymer.*

ELEKTROPREDENA LIGNINSKA NANOVLAKNA

APSTRAKT: *Nanovlakna na bazi lignina predstavljaju značajan potencijal za upotrebu u tehničkim primenama kao održiva alternativa konvencionalnim materijalima. U ovoj studiji ispitivano je elektropredenje ligninskih nanovlakana. Poliakrilonitril (PAN) i polivinil alkohol (PVA) su odabrani kao noseći polimeri kako bi se olakšao proces elektropredenja. Rastvori lignin/polimer sa različitim odnosima mešanja su elektropredeni pod različitim primenjenim naponima. Morfologija dobijenih nanovlakana je okarakterisana pomoću skenirajuće elektronske mikroskopije (SEM). Rezultati su pokazali uspešnu proizvodnju ligninskih nanovlakana bez perli korišćenjem oba noseća polimera. Primetno je da su najfinija nanovlakna dobijena sa PAN-om, dok je upotreba PVA omogućila ugradnju većeg sadržaja lignina (>80%) unutar nanovlakana bez perli.*

Ključne reči: *Elektropredenje, nanovlakna, lignin, noseći polimer.*

1. INTRODUCTION

Electrospun nanofibers have attracted great attention in medical, energy and filtration applications in recent years, because of their specific properties such as high surface area, porosity and possible use of a wide variety of polymers. On the other hand, the use of biomass materials in the production of electrospun nanofibers has become a research focus for the production of sustainable materials. Lignin, which is the second most abundant plant-derived natural polymer after cellulose, is a class of complex polyaromatic biopolymers. The structural complexity and abundance of functional groups in lignin make it a promising precursor for the synthesis of various value-added products, such as high-performance carbon fibers, etc. [1]. It is mainly produced as a byproduct in pulp, paper and bioethanol industries [2]. Although lignin has great potential for biotechnological and industrial use due to the high carbon content, biodegradability, antioxidative activity and thermal stability, a very small portion of the lignin produced is used industrially [3].
Since lignin has a relatively low molecular weight, due to the low viscosity of the lignin solutions electrospinning of lignin yields sprays instead of nanofibers. Therefore, a carrier polymer of a higher molecular weight is generally necessary for electrospinning. In general PAN, PVA or PEO is used as carrier polymers [4]. In this study, lignin nanofibers were electrospun with PAN and PVA with different lignin-to-carrier polymer ratios and different electrospinning voltages. The morphology and fiber diameters of resulting nanofibers were discussed.

2. EXPERIMENTAL

Lignin (softwood alkali lignin, Mw ~10,000 g/mol), PVA (Mw 125,000 g/mol, Mowiol®) and N,N dimethylformamide (DMF, anhydrous, 99.8%) were purchased from Sigma Aldrich. Acrylic based pre-consumer textile wastes were used as PAN polymer precursor. Stock solutions of each polymer were prepared and the mixtures of lignin/PAN and lignin/PVA solutions were prepared in specific mixing ratios. Information on stock solution, mixture ratio and electrospinning parameters were given in Table 1. Nanofibers were produced by NS + NanoSpinner Plus (Inovenso, Türkiye) electrospinning equipment. A 10 mL syringe with a stainless-steel needle (3 cm long, 22 gauge, and flat tip) was used. Produced nanofibers were deposited on a grounded stationary rectangular metal collector covered by a piece of aluminum foil.

Table 1: Polymer solution and electrospinning parameters

Lignin		Carrier polymer			Mixing ratio, v:v (lignin:carrier)	Electrospinning parameters		
Polymer conc.,%	Solvent	Carrier polymer	Polymer conc.,%	Solvent		Voltage, kV	Distance, cm	Feeding rate, ml/h
20	DMF	PAN	20	DMF	50:50 60:40 70:30 80:20	15, 20, 25, 30	15	0.7
30	Water	PVA	10	Water	50:50 60:40	15, 20, 25, 30	15	0.7

The morphology of the resultant nanofibers was characterized using scanning electron microscopy (SEM, Thermo Scientific Apreo S). Each sample was coated with a thin film of gold using a Leica EM ACE600 ion sputtering device. Fiber diameters were determined by using Image J software using SEM images. Fifty measurements were carried out on different parts of each sample.

3. RESULTS AND DISCUSSION

Figure 1 presents the SEM images of lignin/PAN nanofibers fabricated using various lignin-to-PAN solution ratios and electrospinning voltages. Bead-free nanofibers could be obtained by the use of PAN as a carrier polymer at 50:50 and 60:40 solution mixing ratios (except 30 kV electrospinning voltage for 60:40 mixture ratio). The further increase in the ratio of lignin led to the formation of beaded fibers possibly due to the decrease in viscosity by the increase in the lignin ratio. On the other hand, it is worth noting that bead formation is not dominant, most of the fibers were smooth and bead formations were encountered locally in the structure. Therefore, the occurrence of rare bead formation is not expected to significantly hinder the applicability of high-lignin-content nanofibers in technical fields.

	Lignin/PAN solution mixing ratio			
	50:50	60:40	70:30	80:20
15 kV				
20 kV				
25 kV				
30 kV				

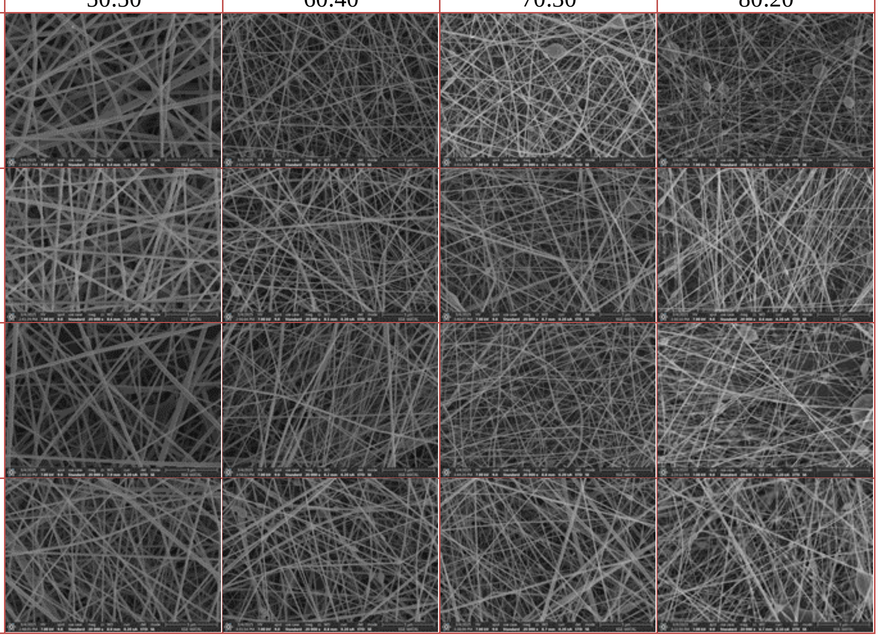

Figure 1: SEM images of lignin/PAN nanofibers

Figure 2 illustrates the SEM images of lignin/PVA nanofibers produced under different lignin: PVA solution mixture ratios and electrospinning voltages. Only two lignin-to-PVA solution ratios could be electrospun (50:50 and 60:40), the increase in the lignin solution ratio led to an increase in viscosity which hindered polymer jet formation during electrospinning process. On the other hand, all the produced lignin/PVA nanofibers were found to be smooth and bead-free. Moreover, although the lignin:PVA solution ratio remained low in the production of nanofibers with PVA, the theoretical lignin mass ratio in the obtained nanofibers was quite high as 75% and 81%, respectively, due to the high lignin solution concentration used (30%).

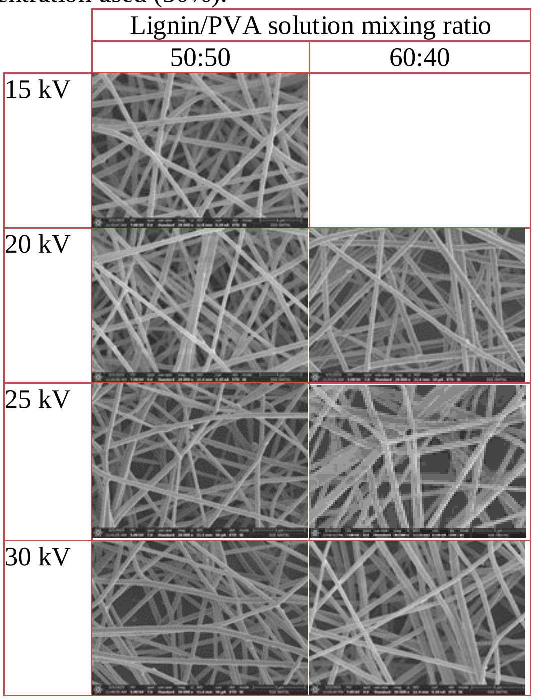

Figure 2: SEM images of lignin/PVA nanofibers

The average diameters of the fabricated nanofibers are summarized in Table 2. For lignin/PAN nanofibers, an increase in the lignin content resulted in a reduction in fiber diameter. At lower lignin ratios, higher electrospinning voltages contributed to a decrease in fiber diameter; however, this effect became negligible at higher lignin concentrations.

Table 2: Mean nanofiber diameters (nm)

	Lignin/PAN				Lignin/PVA	
	50:50	60:40	70:30	80:20	50:50	60:40
15 kV	286.8	144.2	125.7	115.0	485.5	524.6
20 kV	261.4	134.9	127.9	116.4	454.4	544.8
25 kV	254.7	135.8	126.7	113.6	420.2	495.3
30 kV	222.0	133.5	125.3	118.7	433.2	496.0

When PVA was employed as the carrier polymer, thicker nanofibers were obtained. Unlike the lignin/PAN system, increasing the lignin ratio in lignin/PVA nanofibers led to an increase in fiber diameter, because of the increase in solution viscosity. Overall, lower electrospinning voltages tended to produce thicker fibers in both polymer systems.

4. CONCLUSION

Electrospun lignin nanofibers were successfully fabricated using PAN and PVA as carrier polymers. Among the two, lignin/PAN nanofibers exhibited finer fiber morphology in comparison to lignin/PVA nanofibers. In the case of lignin/PAN systems, bead-free nanofibers were obtained at lignin contents of 50% and 60%. However, increasing the lignin content to 70% and 80% resulted in localized bead formation. Conversely, lignin/PVA nanofibers remained bead-free even at higher lignin loadings of 75% and 81%, indicating a higher compatibility of lignin with PVA for producing uniform nanofiber structures at elevated lignin concentrations.

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