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Abstract

In this study, the main aim is to prepare unmodified lignin/water-based polyurethane (WPU) composite coatings with varying lignin concentrations and apply them to polylactic acid (PLA) spunlace nonwoven fabrics (PNFs). The effects of lignin concentrations were investigated in terms of color values, hydrophobicity, air permeability, and antibacterial properties of PNFs. The analysis of chemical groups in the structures of lignin/WPU composite films after curing was performed using Fourier Transform-Infrared (FTIR) spectroscopy, and their thermal properties were analyzed by Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA). The coatings applied to the fabrics were examined by scanning electron microscopy (SEM) through surface images. The fabric coated with the X4 formulation, containing 4% concentration of lignin, displayed the highest water contact angle recorded at 93.6º. As the lignin concentration increased, the air permeability of the fabrics decreased. Regarding color measurements, the PNF sample coated with the X4 formulation showed the highest K/S value of 7.45. In antibacterial activity tests, no inactivation was observed against E.coli bacteria. However, inhibition zone measurements against S. aureus bacteria were 12±1.41 mm and 16.05±0.7 mm on fabrics coated with X3 and X4 formulations having lignin concentration 2% and 4%, respectively. The results indicated that an increase in lignin concentration effectively contributed to the inactivation against S. aureus bacteria. In this respect, this study represents the potential usability of unmodified lignin/WPU coatings providing barrier and comfort properties on biodegradable PNFs.

Keywords: Polylactic acid, Biodegradable, Nonwoven fabric, Composite coatings, Water-borne polyurethane, lignin.

INTRODUCTION

The contemporary textile landscape is witnessing a growing demand for innovative fabrics that prioritize health and well-being, aligning with advancements in material innovation, emerging technologies, and fashion trends (1). While traditional textiles have successfully met primary quality criteria such as biocompatibility, flexibility, and strength, there is a growing demand for textiles with specific functions. Textiles inherently harbor bacteria and fungi, necessitating measures to control their growth. Barrier textiles play a crucial role in environments with a high risk of contamination from infectious or toxic materials, particularly in surgical procedures. Their protective function is achieved through the design and construction of fabrics that shield users from fine particulate matter or liquids. Key qualities include the filtration of medically relevant substances like blood, sweat, and urine. Medical laminates, comprising porous membranes, tissues, and absorbers, limit fluid exchange through capillary flow. Microfiber textiles have proven effective for reusable protective clothing, with nonporous membranes offering the highest level of protection. However, a practical compromise must be struck between barrier function and wearer comfort (2). With the rapid developments in the technical textile sector in recent years, interest in functional textiles has increased. Given the growing importance of sustainability, there is a focus on examining the applicability of natural and biodegradable finishing/coating systems to impart functional effects to textile materials (3,4). During the Covid-19 epidemic, research has been concentrated on the production of bio-based or compostable medical masks, gowns, covers, etc. In addition to these products, there is a focus on developing clothes suitable for daily life. These items are designed to have protective, bactericidal, and virucidal effects (5).

Nonwoven fabrics are utilized in various industrial sectors, including healthcare, agriculture, construction, automotive, aerospace, and more (6). The raw materials commonly used in the medical textile field for nonwoven fabrics are synthetic polymers, such as polypropylene (PP) and polyethylene (PE). Fabrics made from these polymers are not biodegradable in the natural environment, causing environmental issues worldwide (7). The development of nonwoven fabrics is crucial for the production of biodegradable, hygienic, and environmentally friendly sustainable products. Biodegradable polymers play a significant role in this regard, offering a solution to reduce the synthetic waste generated by the textile industry. In recent years, polylactic acid (PLA) has emerged as a natural, biodegradable, and sustainable polymer (5,8) Accordingly, researchers are ongoing with studies on the applicability of hydrophobic and antibacterial finishing/coating on biodegradable PLA nonwoven fabrics. However, the development and application of these functional and protective coatings pose difficulties due to the poor mechanical performance of such natural fabrics (6).

In this way, the possibility of using lignin in functional textiles as an antimicrobial agent has been the subject of research. The lignin polymer exhibits antibacterial activity thanks to the functional phenolic hydroxyl groups in its structure. During this antimicrobial activity, chemical groups inhibit growth by damaging the cell membrane of bacteria, causing hydrolysis and subsequent release of cell contents (9).

Edible films and coatings consist of proteins and polysaccharides present several advantages, including biodegradability, edibility, biocompatibility, aesthetic appeal, effective barrier properties, non-toxicity, environmental friendliness, and cost-effectiveness, as opposed to those

derived from synthetic polymers(10–12) Composite films, incorporating both lipid and hydrocolloid components, have also been formulated. Coating technologies relying on aqueous systems, foam coating, hot melt, or warm melt systems are gaining prominence over older solvent coating processes due to their reduced environmental impact. The development of microporous and hydrophilic polyurethane coatings, along with lamination techniques, has enabled the creation of waterproof and 'breathable' fabrics. The current surge in interest in nano-science and nanotechnology has sparked considerable excitement around nanocoating (10).

Polyurethane (PU) stands out as one of the most versatile polymers in the industry, finding applications in various products like coatings, flexible foams, and elastomers. Polyurethanes (PUs) are highly versatile synthetic polymers widely employed in medical, automotive, and industrial applications. They serve various purposes in furniture, coatings, adhesives, construction materials, fibers, padding, paints, elastomers, and synthetic skins, with a notable presence in the coating industry. PU resins exhibit excellent properties, including abrasion resistance, adhesion, corrosion resistance, weather resistance, low-temperature flexibility, toughness, and superior mechanical strength (13). In the coatings industry, PUs are an important class of polymers due to their good mechanical, chemical, and physical properties. In recent years, there has been significant growth in the development of environmentally friendly water-based polyurethane dispersion (WPUD) products with low toxic properties. These can be used instead of solvent-based PUs containing volatile organic compounds (VOCs) that are harmful to the environment and human health. These environmentally friendly PU systems are employed in paint and pigment systems, drug carrier systems, anti-corrosion, antibacterial, and mechanically resistant coatings, making them important sustainable and environmentally friendly systems in the textile industry. WPUDs exhibit good flexibility, tensile and impact strength. In some studies in the literature, it is reported that various fillers can be added to polymers to enhance the thermophysical and mechanical properties of WPUs, and desired functional properties can be incorporated into the structure (14). Recently, lignin has attracted considerable research interest as a natural polymeric antioxidant and a key ingredient for sustainable materials. Its biodegradability, renewability, wide availability, and remarkable stability have led to extensive study. Researchers are actively exploring lignin's potential in various applications, aiming to utilize its properties for advancing eco-friendly materials and technologies (15,16). The functional groups in the lignin structure can form hydrogen bonds with the urethane groups in PU. By incorporating lignin or lignin-derived natural materials, the mechanical properties of water-based polyurethanes (WPUs) can be improved. This enhancement enables the utilization of PU-based film/coating systems in a wide range of applications that demand durable functional materials, including biomedical, food packaging, automotive interiors, and outdoor applications (16,17). Lignin has high potential for use in lignin-based coating systems where thermal properties and stability are desired, and its usability has been investigated in various fields such as textiles, wood products, non-woven fabric, and packaging systems (18). Lignin, a lignocellulosic material, has been used as a filler to enhance the mechanical and functional properties of polymers (19). The chromophoric, phenolic, ketone, and auxochromic structures in lignin provide effective antimicrobial activity against bacteria and fungi (18,20). The antimicrobial mechanism that lignin can provide is not adequate due to the uneven distribution of the macromolecular size of lignin and the basic monomers of p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol in the structure. On the other hand, the coniferyl alcohol and sinapyl alcohol structures, which are basic monomers, have inhibitory properties against microbes (21). Typically, coatings containing lignin exhibit water contact angles (WCAs) of approximately 80°, with 90° commonly regarded as the threshold for defining a surface as hydrophobic (22). Despite its considerable potential to improve the hydrophobicity, antibacterial activity, and breathability of textiles, there is a scarcity of research on the application of water-based WPU binders, including lignin, as coating/finishing materials (16,19,23).

In one study, the aim was to develop waterproof and breathable fabrics by applying isophorone diisocyanate (IPDI) and a water-based polyurethane (WPU) coating paste containing lignin as an antioxidant material to polyester fabrics using the direct knife coating technique (15). In a separate study, Li et al. employed lignin as a substitute raw material instead of polyhydroxyl components in synthesizing PU macromolecules (24). Zimniewska et al. conducted research on developing nonwoven fabrics that offer functional effects by using nano-lignin-containing coatings (25). They prepared formulations using binding materials, such as kraft lignin-containing silicone emulsion or acrylic dispersion, through an ultrasonic process and applied them to the fabrics. The study revealed that the coating was effective in enhancing the UV protection, antistatic, and antibacterial properties of the fabrics (25,26). Sunthornvarabhas and his colleagues have researched the antimicrobial effects on nonwoven fabrics using lignin obtained from sugarcane. They found that solutions containing lignin transferred onto nonwoven fabrics reduced bacterial colonies on the fabrics due to the increasing concentration of lignin (27). In addition, in another study by this research group, it was reported that a lignin-based coating is more economical for antibacterial activity than coatings using inorganic particles, and lignin is a material with high potential for antimicrobial, antioxidant, ultraviolet protection, and flame-retardant properties. Although it has been accepted that lignin is a natural, biodegradable antioxidant material that can provide antimicrobial and UV protective effects, the potential production of lignin-coated or finished fabrics has not been widely accepted, and scientific

reports on this subject are insufficient. This may be due to the fact that lignin is not recognized as a natural antimicrobial agent by both consumers and manufacturers, attributed to its natural dark brown color (21).

In the existing literature, there are limited research on lignin/WPU composite coatings and their utilization in textile applications. In the previous research, the effect of modified lignin concentration in lignin/WPU composite formulations on the mechanical properties as well as the UV attributes of nonwoven fabrics was studied. The earlier research utilized three-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTMAC), a compound that introduces a positively charged quaternary ammonium group$(NR_4)^+$ into the lignin structure, thereby augmenting its solubility in water (28). This research presents the initial exploration into employing unmodified lignin as functional biopolymer with WPU on coating of PNF and evaluating the antibacterial activity, barrier performance, and comfort properties of textiles. To achieve this objective, various lignin/WPU formulations with differing concentrations of unmodified alkali lignin were prepared. These formulations were subsequently applied onto PNF using a film applicator, followed by thermal curing, and their suitability for PNF was assessed. The characterization studies of lignin/WPU films were conducted through FTIR spectroscopy, TGA, and DSC analyses. Surface analysis of lignin/WPU-coated fabrics was conducted via SEM analysis to examine lignin distribution.

MATERIAL AND METHODS

In this study the base nonwoven fabric type and materials used for preparing WPU/lignin formulations were given in Table 1.

Preparation of WPU Coating Formulations

Water-borne composite coating pastes (solid content: 45%), including WPU binder, unmodified alkali lignin with four different concentrations (1.0%, 1.5%, 2% and 4%) and other additives, e.g. wetting agent, defoamer, thickener and ammonia solution, were prepared as reported in previous study (28). Materials amounts used in this study were given in Table 2. These coating formulations were applied to fabrics using a film applicator (BGD 206/4, Hedef Kimya, Türkiye), which provides homogeneous and adequate coverage on the fabric surface (Fig. 1). Coated fabrics were cured thermally at 135 ºC for 5 minutes. In this study, the curing time in which the fabric form is preserved, and the fixing process is most appropriate was determined as 5 minutes by preliminary studies and was applied for all formulations.

Table 1 Nonwoven fabric type and materials used for preparing lignin/WPU formulations.

Materials	Product name and supplier
PLA spunlace nonwoven (fabric weight of 50 g/m^2)	Mogul Tekstil, Türkiye
Aliphatic polyether anionic waterborne polyurethane dispersion, 60% solid content	Witcobond® 358-90, Lanxess, Germany
Lignin alkali, UV absorber biopolymer	Merck, Germany
Nonionic waterborne blocked isocyanate crosslinker	RUCO®-COAT FX 8041, Rudolf Duraner, Bursa, Türkiye
Wetting agent	NC WET 1200, NC İstanbul Kimyevi Ürünler, Türkiye
Thickener	Pigmacolor Pigmapol PF, Kemiteks, Türkiye
Defoamer	Pigmacolor HC, Kemiteks, Türkiye
Ammonium hydroxide solution	NH_4OH, Kimetsan, Türkiye
Distilled water	

Fourier Transform Infrared (FTIR) Spectroscopy

Various formulations were created, each with different concentrations of lignin, and films approximately 120 µm thick were applied onto glass plates sized 3x120x120 mm using a film applicator. Following this, the films underwent thermal curing at 135°C for 5 minutes. The chemical composition of the films, extracted from the glass plates, was then examined using FTIR spectroscopy (VERTEX 70v Bruker, Germany). FTIR spectroscopy scans were performed across the wavelength range of 400-4000 cm^{-1} with a resolution of 4 cm^{-1} to analyze the thermally cured films.

Differential Scanning Calorimetry (DSC)

The thermal characteristics of cured films were assessed in a nitrogen atmosphere using DSC device (Q20, TA Instruments). Fabric samples weighing approximately 4-5 mg were prepared and housed in aluminum pans for analysis. DSC analysis was conducted in the range of 25°C to 500°C at a heating and cooling rate of 10°C/min. Throughout the analysis, DSC thermograms of the fabric samples were generated. Initially, the sample was heated from 25°C to 500°C at a rate of 10°C/min and maintained at this temperature for 3 minutes

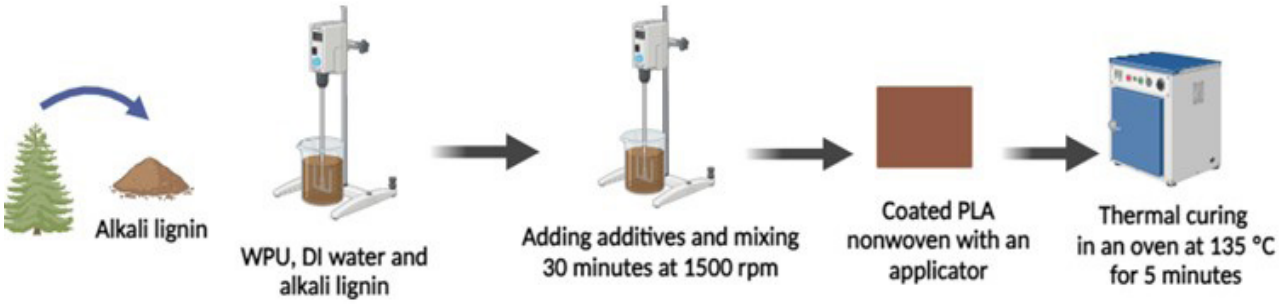


Figure 1 Preparation stage of lignin/WPU composite coating formulations and coating process of PNF.

Table 2 Water-based coating formulations

Code	DI Water	WPU binder	Unmodified lignin	Blocked Isocyanate	Thickener	Dispersing Agent	Defoamer	Ammonia Solution
X	18.61	75	0	2	2.63	0.75	0.46	0.55
X1	18.61	75	1	2	2.63	0.75	0.46	0.55
X2	18.61	75	1.5	2	2.63	0.75	0.46	0.55
X3	18.61	75	2.0	2	2.63	0.75	0.46	0.55
X4	18.61	75	4.0	2	2.63	0.75	0.46	0.55

to eliminate any thermal or mechanical transition traces in the fabric material. Subsequently, the sample was cooled to 25°C at a cooling rate of 10°C/min, concluding the analysis. This procedure was repeated to acquire DSC thermograms for all fabric samples.

Thermogravimetric Analysis (TGA)

The thermal resilience of the films was examined using a TGA apparatus (Exstar SII TG/DTA7300) under a nitrogen atmosphere. The assessment was carried out at a flow rate of 50 ml/min and a heating rate of 10 ºC/min across the temperature span of 25 to 800 °C (29).

Scanning Electron Microscopy (SEM)

The SEM images of uncoated and coated fabrics were captured utilizing SEM device (FE-SEM, Hitachi, Regulus 8230) operating at 10.0 kV with a magnification of x100. Before observation, a thin layer of gold was deposited onto the fabric's surface to provide the electrical conductivity of the fabric samples.

Color Measurements

To assess the photometric attributes of the thermally treated PLA nonwoven fabric samples after coating, the CIE Lab* color values were acquired using a spectrophotometer (X-Rite, CI7800, Switzerland). The CIE L*a*b* color space has a lightness/darkness component (L*), a* component (green-red axis), and b* component (blue-yellow axis). Values of the L* component can be obtained in the range from 0 to 100 (0-black, 100-white). C* (chroma) refers to the saturation of the color at a certain L* value, and h° (hue) refers to the shade of the color. The ratio between absorption coefficient (K) and scattering (S) is known as color yield and is calculated with the following equation (1)(30).

$$\frac{K}{S} = \frac{(1-R)^2}{2R} \quad (1)$$

Surface Wettability Measurements

The surface wettability of the different samples was characterized via measuring water contact angle (WCA), which is a quantitative measure of the wetting of a solid with a liquid. The device of choice for measuring contact angles and dynamic contact angles is an optical tensiometer(31). The contact angle is an indicator that provides an understanding of the wettability properties of the materials and therefore is effective in determining the waterproof properties of the materials(32). The hydrophobic character of PNF fabrics was determined by an optical tensiometer device (Attension Theta Flex, Biolin Scientific, Sweden). The fabric specimens were sectioned as 2 cm^2 and affixed to the glass surface using double-sided tape. Subsequently, a droplet of 5 µL distilled deionized water was dispensed onto the fabric from a micro-syringe, and images were taken to quantify the angle established at the interface between the liquid and solid phases. The CA left and right measurements was conducted after the drop release (CA-$T_{0\text{-}10}$ sec) and mean CA values were calculated. Each sample was measured on five different points and the average values were calculated.

Air Permeability Measurements

The air permeability properties of PNFs were evaluated using an air testing apparatus (MO21A, SDL ATLAS, Switzerland) according to the specifications outlined in TS 391 EN ISO 9237 "Determination of air permeability of textile fabrics." This procedure entails measuring the volume of air passing through 1 m^2 of fabric per minute under a water pressure head of 10 mm. Air permeability tests were applied to 20 cm^2 uncoated and coated fabric samples with 100 Pa pressure increase and recorded in $l/m^2/s$ (33).

Antibacterial Activity

The effect of lignin concentration on the antibacterial activity of WPU/lignin coated PNFs was investigated against gram-positive (Staphylococcus aureus: ATCC 25923) and gram-negative (Escherichia coli: ATCC 25922) bacteria using agar disc diffusion method according to test standard of PN-EN ISO 20645:2006 (34). The susceptibility of bacteria to antibiotics was determined on MH (Mueller Hinton) agar by Kirby–Bauer disk diffusion technique. Sterile loops were employed to retrieve samples from the bacterial colonies that had developed as distinct entities on the culture plates. These samples were then introduced into MH broth and allowed to incubate for a period of 1-2 hours at 37ºC. Once turbidity became evident, a standardized level of turbidity was achieved by calibrating to McFarland 0.5 (equivalent to 108 microorganisms/ml). This resulting suspension was subsequently used for broad-spectrum cultivation on MH agar medium using a sterile swab. WPU/lignin coated fabrics prepared as 1 cm2 were placed in the medium with sterile forceps. Gentamisin was used as a positive control. After incubation of petri dishes at 35-37ºC for 18-24 hours, inhibition zone diameters were measured.

RESULTS AND DISCUSSIONS

Fourier Transform Infrared (FTIR) Spectroscopy

The presence of chemical groups in the FTIR spectra of the clear WPU film (formulation X) and lignin/WPU polymeric films (formulations X1 and X4, with 1% and 4% lignin concentrations, respectively) was identified by absorption peaks (Fig. 2). Examination of the FTIR spectra of films prepared at different lignin concentrations revealed the original functional groups of WPUs. C-O-C stretching absorption peaks at 1236 cm^{-1} were observed, as expected. In the X4 formulation with a high lignin concentration, the intensity of these peaks slightly increased in the spectrum due to interactions between lignin and WPU (35). The stretching vibration peak, which represents the ester group, occurred at 1720 cm^{-1} peak in all polymeric films (29). During FTIR analysis, a higher transmittance percentage at a specific wave number in the spectra obtained from the cured film sample indicates a limited presence of functional bonds within the polymer material structure. These bonds absorb light emitted from the device to the sample. Thus, the reduction in transmittance percentage is associated with the formation of a cross-linked polymer structure due to thermal curing (36).

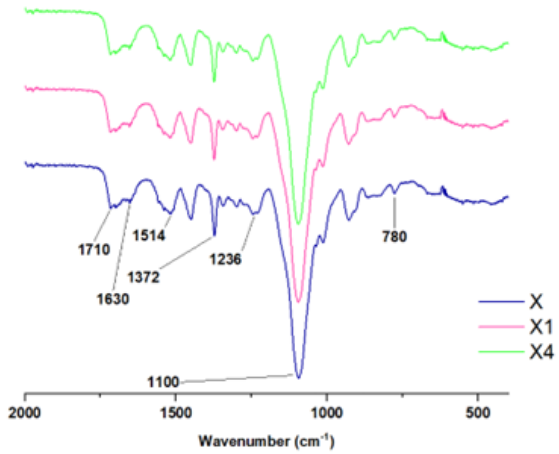


Figure 2 FTIR spectra of thermally cured films.

Differential Scanning Calorimetry (DSC)

DSC analysis results of thermally cured films were given in Table 3. In Table 3, DSC analysis results of X, X1 and X4 films prepared with %0, 1.0 % and 4.% lignin concentrations, respectively were given. According to the results, the glass transition temperatures (Tg) and melting temperatures (Tm) of the films obtained with the X1 and X4 formulations prepared at 1% and 4% lignin concentrations, respectively, were higher than the Tg and Tm values of the films prepared with the lignin-free X formulation. The results show that more energy is required to break the interaction between lignin and WPU in lignin/WPU composite films prepared at high lignin concentration, and Tg and Tm values increase accordingly (29). DSC thermograms of X4 and X films were shown in Fig. 3.

Table 3 Thermal analysis results of cured unmodified lignin/WPU films.

Sample Code	T_g (°C)	$\triangle H_{mTg}$ (J/g)	T_m (°C)	$\triangle H_{mTm}$ (J/g)
X	323.53	26.43	396.02	56.50
X1	358.49	16.56	411.35	57.24
X2	359.30	17.56	412.24	67.30
X3	361.25	17.97	411.38	71.50
X4	365.42	18.43	413.82	80.53

Thermogravimetric Analysis (TGA)

TGA analyses were conducted to assess the impact of lignin concentration on the thermal stability of lignin/WPU composite films, with results presented in Table 4. The thermal degradation of lignin typically occurs in three stages. The initial step involves the separation of the ether bond, followed by dealkylation and cleavage of the C-C bond in the second stage. The final step entails carbonization demethylation. As the ether bonds break, carbonaceous structures undergo rearrangement to form more conjugated structures, leading to a high degree of graphitization through various cross-linking reactions (9). Lignin/WPU composite film prepared with X4 formulation containing 2% lignin exhibited better thermal stability than the film prepared with lignin-free X formulation and X1 film prepared with the formulation including 0.5% lignin. Initial decomposition and maximum decomposition temperatures were obtained as 305.15 °C and 419.13 °C for the X film, 312.12 °C and 428.73 °C for the X1 film, 341.33 °C and 446.51 °C for the X4 film. The increase in the initial degradation temperature seen in the composite film that incorporates lignin and WPU can be ascribed to the greater energy requirement needed to disrupt the molecular linkage between the lignin and WPU chains (29,37). According to the results obtained from the X4 film, the initial decomposition temperature of the film obtained from the lignin-free X formulation was 12% and maximum decomposition temperature increased by 6.5%. TGA curves of X4 and X films were shown in Fig. 4.

Table 4 TGA results of cured films.

Sample code	T_{onset}(°C)	T_{max} (°C)	Weight loss (%)
X	305.15	419.13	97.68
X1	312.12	428.73	96.33
X2	326.30	434.56	96.21
X3	336.56	444.22	93.50
X4	341.33	446.51	89.80

As seen in Table 4, as a result of using higher lignin concentration, the maximum decomposition temperature for the film prepared with X4 formulation was obtained as 446.51 °C and which is higher about ~27 °C than the maximum decomposition temperature of the X film (419.13 °C). Within the films crafted using the X, X1, and X4 formulations, weight losses of 97.68%, 96.33%, and 89.80% were observed, respectively. The incorporation of lignin enhanced the thermal resistance of these formulations and improved their stability, yielding an 8% decrease in weight loss for the X4 formulation

when contrasted with the X formulation.

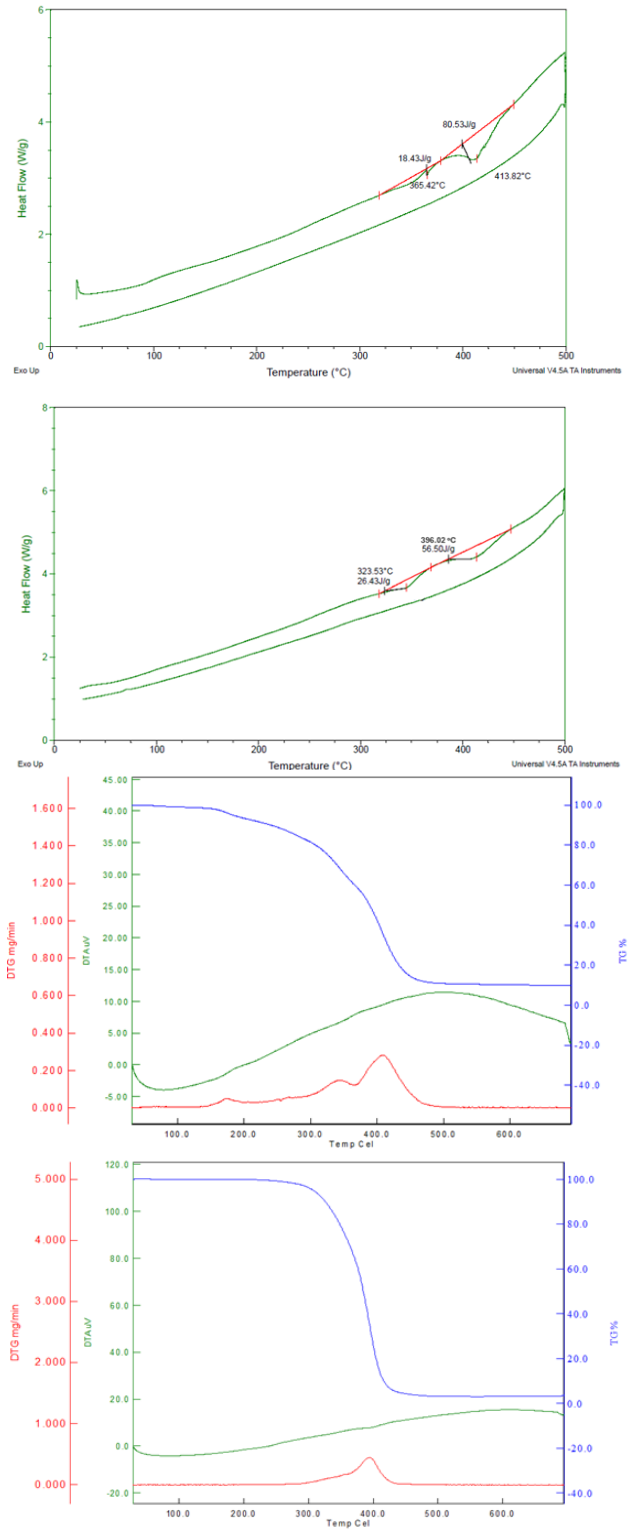


Figure 4 TGA curves of a) X4 and b) X films.

Scanning Electron Microscopy (SEM)

FE-SEM images of thermally cured PNFs prepared with formulations X, X1 and X4 containing lignin at different concentrations were given in Fig. 5.

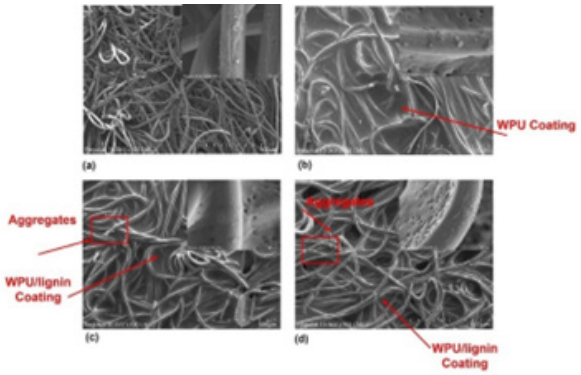


Figure 5 FE-SEM micrographs of (a) uncoated fabric, (b) X (WPU), (c) X1 (L/WPU 1%), (d) X4 (L/WPU 4%).

SEM images of coated and thermally cured PNFs were compared with the image of pure PNF. When the FE-SEM images are examined, it is seen in Fig. 5(a) that the uncoated nonwoven fabric structure has a porous network structure and has a rough, uneven surface due to the entanglement of the fibers. In Fig. 5(b), it was observed in the surface image of the PNF, coating formulation filled the spaces between the fibers and the surface had a more homogeneous structure. The surface appearance of fabrics coated with formulations X1 and X4 containing 1% and 4% lignin, respectively, were given in Fig. 5(c) and Fig 5(d). The gaps between the fibers in the fabric structure are filled with coating material to a large extent. The function of the fillers used in hybrid coatings prepared with the combination of different materials depends on the uniform distribution of these materials in the polymer(38). Therefore, the distribution of WPU-based coatings containing different concentrations of lignin on the fabric surface was evaluated with FE-SEM images. As a result of the application of WPU/lignin coatings and pure WPU coating paste to the fabric surface, the surface images were examined comparatively (Fig. 5(c)–(d)). It can be seen from Fig. 5 (b) that the surface of the pure WPU coated and thermally cured PNF fabric is more homogeneous and the gaps between the fibers are filled with coating paste. Some differences were observed in the appearance of the coating applied to the fabric with the incorporation of lignin particles into the WPU dispersion. A restricted number of white dots, highlighted by red rectangles in the images, became evident on the surface of the PNFs coated with WPU/lignin coating (Fig. 5(c)-(d)). As can be seen, the lignin particles were almost evenly dispersed in the WPU dispersion, only minor agglomerations were observed in some parts. The lignin included in the formulation filled the space between the fibers to reduce surface porosity. At the meantime lignin can expose the hydrophobic surface to resist moisture(39). The homogeneous coating formed on the fabric surface with the increase in lignin concentration, given the surface a hydrophobic feature, also supported this by the WCA measurement results. The lignin added to the WPU dispersion increased the adhesion between the fiber and the binder, therefore strengthened the interaction between the layers forming the multilayered networks. Aggregations formed by the addition of lignin to the WPU dispersion can be associated with the density of hydroxyl groups in the medium due to the increased lignin content(40). In Fig. 5(c) and Fig.

5(d), it can be observed that the lignin particles are evenly dispersed in the WPU. This homogeneous dispersion may result from a balanced adjustment of the mixing speed and time of WPU/lignin dispersion(41). It can be seen from Fig. 5(d) that the 4% by weight lignin in the coating paste appears to clump together in some areas. This is due to the fact that the high concentration of lignin flocculates to form large particles during mixing in the WPU. There is an obvious phase interface between the lignin particles and the WPU resin. The low lignin content WPU/lignin coating and WPU coating are very homogeneous and the agglomerated lignin particles are very few in the 1% lignin content coating, indicating a homogeneous structure of the WPU coating(42).

Color Properties of Coated PNFs

The results of CIEL*a*b* color values were given in Table 5. One of the problems encountered with the application of lignin in WPU materials is the dark color of lignin due to its natural structure, which can limit some applications such as coatings(43). Lignosulfonate staining results in color alteration during the dyeing procedure, and managing this staining is challenging. Sulfonated kraft or alkali lignin obtained from pulping processes tend to contain a higher concentration of chromophores, leading to a deeper coloration(18).

Table 5 CIEL*a*b* color value results of coated PNFS.

Sample code	L*	a*	b*	C*	h°	K/S
X1	81.09	7.57	37.66	38.41	78.64	2.78
X2	77.03	10.21	39.25	41.36	72.26	6.7
X3	63.29	16.73	44.38	47.43	69.34	7.12
X4	49.14	19.88	30.13	36.10	56.59	7.45

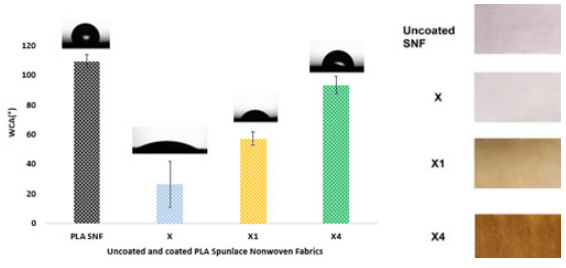
In its natural state within wood, lignin appears nearly colorless; however, industrial variations like alkali lignin or lignosulfonate exhibit a deeper hue. The creation of chromophores is a consequence of both the extraction of lignin and the pulping processes; however, the precise mechanism behind their development remains uncertain. Several recognized chromophore configurations encompass: (1) aromatic rings with conjugated carbon-carbon double bonds; (2) quinone methides and quinones; (3) chalcone structures; (4) unpaired electrons (free radicals); (5) metal complexes featuring catechol structures. The contents of the quinone methide and quinone structures are in low amount but contribute most of the lignin color. The deep hue exhibited by industrial lignin is also regarded as a limitation in the advancement and widespread adoption of products derived from lignin (44). Nevertheless, the inherent dark hue of technical lignin remains an obstacle in realizing its potential for enhanced value in various applications, such as dyestuff dispersants. To encourage the utilization of high value-added lignin, the crucial step involves achieving an acceptable light tint for the lignin (45). As shown in Fig. 4 (b) in this study, the color of the WPU coated nonwoven fabric changed in the dark direction as the amount of lignin increased. In fabrics coated with composite formulations, the L* light-darkness value of the fabric decreased with the increase in the lignin concentration in the coating paste, that is, the fabric changed to a darker color from light brown to dark brown. As the lignin concentration increased, the redness values (a*) of the fabric increased, the yellowness (b*) values decreased, and the K/S color yield values increased. Color tone values (h°) were observed in the region with high redness (a*) between a+ and b+ axes and close to the x-axis.

Wettability Measurements of Coated PNFs

In WCA measurements, the wettability properties of uncoated PNF and thermally cured PNFs that were coated with WPU/lignin formulations containing different concentrations of lignin were tested and the WCA results given in Table 6. The water repellency of the coated PNF surfaces was assessed by calculating the water contact angle (WCA) through the application of a water droplet on the fabric surface. The images captured using an optical tensiometer device are depicted in Fig. 6. As a result of the wettability test, the WCAs of the fabrics were determined and the hydrophobic and hydrophilic properties of the surfaces were evaluated. According to the test results, while the raw PLA fabric had a WCA of 109.7° and was measured as 26.2° for the pure PU coated PNF. The WCA value of lignin-free WPU coated fabric decreased considerably. This low WCA indicates that the surface has a hydrophilic character. In contact angle measurements, the size of the contact angle formed between the water droplet and the surface gives information about the hydrophobicity of the surface(46).

Table 6 Surface wettability measurements of fabrics; SD, standard deviation.

Samples	WCA left [°]	WCA right [°]	WCA mean [°]
PNF	110.3	109.2	109.7
PNF (± SD)	9.57	2.40	5.06
X	23.2	29.2	26.2
X (± SD)	3.15	31.8	15.6
X1	58.6	57.1	57.8
X1 (± SD)	4.7	4.5	4.6
X2	61.6	61.9	61.7
X2 (± SD)	5.7	5.5	5.6
X3	78.6	77.1	77.8
X3 (± SD)	5.7	6.5	3.6
X4	91.9	95.3	93.6
X4 (± SD)	8.3	5.1	6.0



(a) (b)

Figure 6 (a) Water contact angles and (b) photographic images of fabrics.

The water absorption capacity and WCA at the surface are related to the energy of the surface and the pore size at the surface. The reduction in water absorption and the large degree of WCA behavior can be explained by the reduction of the pore size on the surface(47). In pure WPU coating, it can be said that the coating exhibits wettability due to the hydrophilic groups in the structure of WPU(48). It was observed that the hydrophobic properties of the coatings improved with the addition of lignin at increasing concentrations to the WPU-containing formulation. Upon integrating 1% lignin into the WPU formulation, a significant enhancement in the water contact angle (WCA) value on the lignin/WPU coated fabric surface was observed, reaching 57.8°. This value demonstrated a remarkable improvement of 95.5% compared to the WPU coating without lignin. The WCA of the coated fabric surface was measured as 93.6° when the lignin concentration was used at a low density such as 4% in formulation X4 which was the WCA is 64.7% higher than that of X1 formulation including 1% lignin. According to these results, the WCAs of lignin/WPU coatings increased gradually with the increase in lignin concentration and this improved the hydrophobic property of the pure WPU coatings. The formulation X4, containing 4% lignin concentration, achieved the highest WCA value of 93.6°. These findings indicate the effective hydrophobic capability of the lignin/WPU coatings, primarily owed to the inherent qualities of lignin within the WPU formulation(49,50). The water contact angles (WCAs) of coatings containing lignin typically range around 80°. A threshold of 90° is often used to categorize a surface as hydrophobic (22). Lignin can form a moisture resistant hydrophobic surface by capping the hydrophilic groups in WPU. It can be said that the uniform and dense coating formed with hydrophobic lignin particles dispersed in the WPU matrix on the PNF surface provides good barrier properties against water with a WCA value of 93.6° (39).

Air Permeability Measurements of Coated PNF

The results of air permeability properties for thermally cured fabrics were presented in Table 7. SEM images (see Fig. 5(a)) reveal that the PNF exhibits a porous and open structure.

Table 7 presents the air permeability results. The neat PLA nonwoven fabric, with its open porous structure, exhibits high air permeability, measured at 1287 l/m^2/s. Coating the fabric with lignin/WPU composite formulations yields varied air permeability: 290 l/m^2/s for the X1 formulation containing 1% lignin and 142 l/m^2/s for the X4 formulation containing 4% lignin. This coating facilitates the formation of a denser cross-linked structure between the PLA fibers and the lignin/WPU composite coating, effectively closing gaps between fibers (51). The comfort aspects of wearable devices are influenced by intricate interplays among fabric permeability, flexibility, climatic conditions, physiological responses, psychological factors, and design attributes. Clothing comfort can be influenced by a blend of variables, including temperature, humidity, air circulation, and analogous elements. Due to the desired protective feature of medical gowns used in the medical textile category, air permeability is the main determining feature for wearing comfort. In most cases, medical gowns designed for superior liquid barrier performance tend to exhibit low air permeability but are often uncomfortable due to their limited air permeability(52). A surgeon working at a moderate pace at 20 °C will feel comfortable in his/her surgical clothing, provided that the fabric has an air permeability of at least 100 l/m^2/min (53). The structure of the coating paste restricts air passage by closing available voids in the fabric structure, leading to decreased breathability values with increasing lignin concentration in PNFs coated with lignin/WPU composite formulations (54,55).

Antibacterial Activity Analysis of coated PNFs

In the antibacterial activity analysis, uncoated (control sample) and coated fabrics were tested against to E. coli and S. aureus. While PNF coated with lignin/WPU formulations did not show antibacterial activity against E. coli bacteria, the sample containing 2% and 4% lignin showed antibacterial activity against S. aureus bacteria. Diameters of inhibition zones were measured as 12±1.41 and 16,05±0.7 mm against S. aureus bacteria in PNF coated with X3 and X4 formulations, respectively (Fig. 7). The antibacterial potential of lignin arises from its phenolic structure, which also serves as the primary origin of its antioxidant capabilities. Typically, gram-negative bacteria exhibit greater resilience to lignin compared to gram-positive counterparts, although this tendency can be influenced by the specific structural attributes of lignin. However, the documented antibacterial efficacy of lignin generally falls short of that achieved by commercial antibiotics. Studies concerning the antifungal and antiviral effects of lignin are scarce. Consequently, further research is imperative to enhance and optimize lignin's antimicrobial properties (56).

Lignin has antioxidant properties to protect against possible risks of free radical species (ROS). It exhibits notable antimicrobial effectiveness against both bacteria and fungi. The varying degrees of responsiveness between Gram-positive and Gram-negative bacteria to antibacterial agents can be attributed primarily to the divergent cellular compositions of these bacteria. Gram-negative bacteria possess cell membranes composed of lipopolysaccharides, lipids, and proteins, caused in a more confined scope of inhibition. As a result, greater efficacy in terms of antimicrobial action can be observed against S. aureus, a Gram-positive bacterium, in comparison to E. coli (6).

Table 7 Air permeability values of thermally cured fabrics coated with lignin/WPU composite formulations.

Sample code	Uncoated PNF	X1	X1	X3	X4
Air permeability (l/m^2/s)	1287	290	265	238	142
CV (%)	3.6	10.0	8.0	11.0	10.1

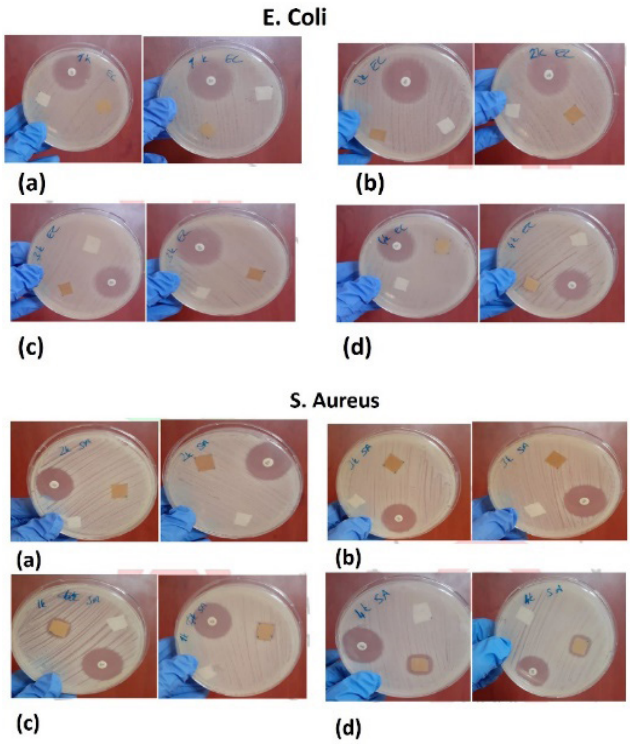


Figure 7 Diameters of inhibition zones of uncoated white PLA nonwoven fabrics (X) and light brown fabrics coated with a) X1, b) X2, c) X3 and d) X4 formulations against to E.coli and S. aureus bacteria.

CONCLUSION

This study involved the preparation and successful application of unmodified lignin/WPU composite coating formulations, featuring four distinct lignin concentrations, onto PNFs. According to color measurement results, it was observed that increasing lignin concentration in the lignin/WPU formulations led to higher redness values, decreased yellowness values, and increased K/S color yield values. The PNF sample coated with formulation X4, containing a lignin concentration of 4%, achieved the highest K/S value (7.45). When the wettability measurements results are evaluated according to the WCA values of the surfaces of coated and thermally cured PNFs, WCA values increased with the increasing lignin concentration in lignin/WPU composite coating pastes. The lowest WCA value of 26.2° was obtained with the lignin-free formulation X. On the other hand, the highest WCA value of 93.6° was obtained with the formulation X4 including 4% lignin. WCA values of the lignin/WPU coatings demonstrated a gradual increase as the concentration of lignin was elevated. Remarkably, the X coating without lignin also exhibited improved hydrophobic properties. These findings emphasize the noteworthy hydrophobic performance of the lignin/WPU coatings, largely stemming from the intrinsic qualities of lignin within the WPU formulation. SEM analysis revealed that the Lignin/WPU composite coating paste filled gaps between fibers on the PNF surface, resulting in a more uniform appearance. In the DSC analyzes, it was concluded that the use of lignin in varying concentrations in lignin/WPU composite formulations improved the thermal properties of the films compared to the film prepared with the lignin-free X formulation. According to the TGA analysis results in which the thermal stability of the composite formulations were analyzed; lignin/WPU films exhibited better thermal stability than the lignin-free X film. Initial decomposition and maximum decomposition temperatures of X4 film reached of 341.33°C and 446.51°C, respectively, and these values were obtained as 305.15°C and 419.13°C for the lignin-free X film. The increase in thermal stability is attributed to the cleavage of C–C bonds in the lignin structure and degradation of aromatic rings. Additionally, in TGA results, the weight loss for the X4 formulation decreased by 8% compared to the lignin-free X film. Comfort tests indicated that the air permeability of PNF, owing to its open porous structure, measured at 1287 l/m2/s. Coating with the X1 formulation yielded an air permeability of 290 l/m2/s, while the X4 formulation, containing 4% lignin, resulted in a measurement of 142 l/m2/s. The reduction in air permeability in fabrics coated with high lignin concentration formulations is attributed to the lignin/WPU structure filling the pores between fabric fibers, thus impeding air passage. Moreover, results of the antimicrobial activity demonstrated the efficacy of li gnin/WPU co atings on PN Fs ag ainst microorganisms such as S. aureus This study showed that lignin, a natural biodegradable polymer, can impart different functional properties to PNF fabrics. The findings of this study are anticipated to provide valuable insights into the development of sustainable and functional materials for various applications, contributing to the advancement of eco-friendly solutions in the textile industry.

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