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Research Article

Ultraviolet Protection and Antibacterial Properties of Polylactic Acid Nonwoven Fabrics Coated with Water-Borne Polyurethane/Zinc Oxide Composite Coatings

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ABSTRACT

This study aimed to create thermally curable, water-borne polyurethane/zinc oxide (WPU/ZnO) composite coating pastes with varying ZnO concentrations. ZnO nanoparticles were synthesized using a wet chemical process, and the resulting WPU/ZnO coating pastes were applied to PLA nonwoven fabrics (NWFs). In characterization studies, differential scanning calorimetry (DSC), scanning electron microscopy (SEM), Fourier transform-infrared (FTIR) spectroscopy, and X-ray diffraction (XRD) analyses were conducted. Ultraviolet (UV) protection and antibacterial activity of fabrics were investigated. With WPU/ZnO composite coatings, the UV protection properties of the coated fabrics were enhanced compared to the uncoated fabric. The highest UPF value of 53.57 was obtained with the fabric coated with the formulation containing a ZnO concentration of 10%. This fabric also demonstrated more effective antibacterial activity against both S. aureus and E. coli bacteria. Inhibition zone diameters against E. coli and S. aureus bacteria were measured as 15.5 ± 0.70 mm and 18.25 ± 0.35 mm, respectively. The results of this study illustrate that functional composite coatings for bio-based NWF structures hold great promise for producing effective UV protective and antibacterial materials, potentially setting the stage for future applications.

1. Introduction

Nanotechnology is an precise arrangement of atoms and molecules to fabricate functional materials, devices, and systems on a nanometer scale, generally spanning from about 0.1 to 100 nanometers. This level of control leads to the development of structures with outstanding properties. Nanomaterials possess distinctive optical, mechanical, catalytic, and biological properties. These characteristics have gained the interest of researchers in the textile industry, rapidly increasing the exploration of nanotechnology in this domain. Textiles are a prime application area for nanotechnology due to the potential to enhance functional properties. Metallic nanoparticles (NPs) are extensively studied for their integration into textiles, improving properties like water and soil resistance, wrinkle resistance, antimicrobial action, antistatic properties, UV protection, and flame resistance [1, 2].

Metal oxide particles are used in textiles especially for their antibacterial properties. There are different incorporating approaches of them onto textiles. The effectiveness of antimicrobial action on textiles depends on factors such as the type, nature, concentration, and application method of the antimicrobial agent [1]. The researches suggests that metal NPs hold promise for creating antimicrobial fabrics. However, despite their remarkable efficacy against microorganisms, the industry's utilization of silver and gold nanoparticles as antibacterial agents is restricted due to their high cost. In contrast, metal oxide NPs such as ZnO, copper oxide (CuO), and magnesium oxide (MgO) are now commonly used in the textile industry to produce functional textiles [2].

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Inorganic nanometal oxides like ZnO, titanium dioxide, and MgO are safe for both humans and animals. Among these oxides, ZnO has captured attention in textile research because of its affordability, easy accessibility, and distinctive chemical and physical attributes. Nano ZnO finds applications in various technologies such as photocatalysis, solar cells, sensors, displays, anti-reflection coatings, sunscreens, UV absorbers, piezoelectric devices, and more [2]. ZnO is bio-safe, biocompatible, and applicable in biomedical uses. These unique features position ZnO as a highly significant nanomaterial for future research and applications [3].

ZnO is recognized as safe by the United States Federal Drug Administration [4]. Therefore, ZnO nanoparticles function as essential ingredients for cosmetics, polymers, food packaging, medicine, and more, contributing a range of versatile functional properties. Recent years functional textile fabrics have been advancing with the integration of nano ZnO, offering safeguard against harmful UV rays and aiding in the prevention of sunburn, skin cancer, and allergies resulting from excessive UV exposure [2].

ZnO NPs are applied to textiles using methods like composite spinning or finishing approaches [5]. ZnO-functionalized textiles can be created through methods like dip-coating, sol-gel, padding, electro deposition, and chemical bath deposition. These techniques deposit nano- and micro-sized ZnO onto textiles using prepared suspensions or in situ synthesis [4]. Various polymers, like polyurethane (PU), poly(vinylidenechloride) and polyethylene are used to laminate or coat textiles. PU coating stands out for its multifunctionality, offering precise mechanical, physical, biological, and chemical properties, as well as excellent flexibility and thermophysiological comfort. [6]. Recently, eco-friendly water-borne polyurethane (WPU) dispersions, have become popular. Incorporating nanofillers or biopolymers into polymer matrix improves its thermophysical and mechanical properties and offers extra functional advantages to the coated surfaces [7-11].

The global monthly consumption and disposal of medical products, driven by COVID-19 and similar illnesses, reaches 130 billion items. These disposable products, typically made from polyester, polyethylene, and polypropylene, degrade slowly and harm the environment. Switching to eco-friendly, biodegradable materials is essential. PLA, a biodegradable polymer, is emerging as a viable alternative. It is affordable, widely available, and used in various industries, making it a valuable option for improving disposable medical textiles like masks, covers, and aprons [12]. In the current literature, synthetic nonwovens are predominantly used, with cotton fabrics being less common, for creating functional surfaces with ZnO. In one study, Nikiforov et al., employed a three-step atmospheric pressure plasma process to create polyethylene terephthalate (PET) NWFs with three types of NPs: AgNP, CuNP, and ZnONP. All nano fabrics exhibited strong antimicrobial effects on E. coli and S. aureus. Notably, CuNPs were nearly as effective as AgNPs, while ZnONPs showed lower efficiency against S. aureus [13].

Ramamurthy et al., reported PP hydroentangled NWF's antimicrobial properties. They initially etched the NWFs using RF plasma. Following this, they applied nano-scale coatings of ZnO and CuO using KrF excimer-based PLD. The team then conducted morphological and antimicrobial analyses to comprehend the antibacterial mechanism of the coated fabrics. These coatings exhibited enhanced activity against the gram-positive S. aureus compared to the gram-negative E. Coli [14].

In another study, polyacrylonitrile and poly (vinylidene fluoride) (PVDF) based nanofibrous nonwoven were created through electrospinning by Dong et al. In order to introduce antibacterial properties, ZnO NPs were covalently bonded to the PVDF nanofibers. The obtained nonwoven structure demonstrated effective antibacterial function and maintained good anti-wash properties [15]. Ferreira et al., investigated the properties of PP NWF, focusing on structure, physicochemical aspects, and comfort. They functionalized intermediate layer fabrics with ZnO NPs at 0.3% and 1.2% by using electrospinning, dip-pad-dry, and exhaustion methods. The samples were tested for antimicrobial properties. A three-layered structure was then assembled and thermoformed

into facemasks, which were evaluated for antimicrobial effectiveness, filtration efficiency, and breathability [16]. Tania and Ali investigated the impact of nano ZnO coatings on cotton fabric and obtained results were compared to uncoated fabric. ZnO nanoparticles were applied with and without an acrylic binder using a mechanical thermo-fixation technique.

Antimicrobial activity, UV protection, crease resistance, and mechanical properties like tensile strength, tearing strength, bending length, and frictional resistance were assessed. The findings indicated that the binder significantly affects nanoparticle deposition and enhances both functional and mechanical properties, with the binder-coated fabric demonstrating superior performance against microorganisms [17]. Zhang et al., used a simple ion exchange method to create ZnO nanoparticle-coated calcium alginate NWF. They immersed alginate NWF in $Zn(NO_3)_2$ solution for ion exchange, followed by amino hyperbranched solutions to prepare ZnO NPs. The results showed a consistent, high-density ZnO NP coating on the alginate NWF [18]. Deng et al., used magnetron sputter coating to deposit Al-doped ZnO (AZO) films on PET spunbonded nonwovens, and the AZO films showed enhanced UV absorption properties [19].

Adding antimicrobial features to protective gear can greatly reduce pathogen contamination and help mitigate healthcare-associated infections. In a study, PP NWF, commonly used in personal hygiene products and hospital protective gear, was surface-modified using corona treatment. Dyne liquid assessed the surface polarity, showing increased polarization. The polarized PP NWF was then coated with ZnO antiviral agents via a spray method, using a polyurethane solution as an adhesive. The study focused on the antiviral and antibacterial activities of the coated fabric against MS2 bacteriophage, S. aureus, and Klebsiella pneumoniae. The polyurethane binder minimized antiviral coating leaching, and the fabric achieved a 99.90% reduction in microorganisms after 24 hours [20]. Uğur et al., prepared multilayer nanocomposite films with ZnO nanoparticles on cationized woven cotton fabrics using a layer-by-layer molecular self-assembly method. Cotton fabrics were pretreated with 2,3-epoxypropyltrimethylammonium chloride (EP3MAC) to impart a cationic surface charge. These films showed excellent antimicrobial activity against Staphylococcus aureus and improved UV protection for the fabrics [21].

Recently, there has been an increasing attention in research focused on developing biodegradable medical textiles to enhance sustainability. In this context, it is crucial to functionalize textile surfaces made from natural and biodegradable materials using environmentally friendly materials and cost effective methods to explore their potential use in medical textiles. In recent years, PLA based nonwoven substrates have gained attention to develeop functional textile surfaces. In the literature, Zhang et al., prepared PLA/ZnO/additives non-woven slices by melt blending method. These fabrics showed good hydrophobicity and antibacterial properties [22].

In previous studies, functional properties of PLA fabrics were examined by applying lignin/WPU composite coatings using both unmodified lignin [8] and modified lignin biopolymers [9], as well as lignin/ZnO/WPU-based composite coating formulations combining lignin biopolymer with ZnO metal oxide [10]. In previous study, lignin/ZnO/WPU coatings on PLA nonwoven fabrics enhanced antibacterial properties, tensile strength, abrasion resistance, and UV protection and presented potential of this study for medical textiles applications. UV absorption ability of lignin biopolymer provided excellent UV protection to PLA fabrics. Color properties, air and water vapor permeability performances and surface wettability measurements of coated PLA fabrics were also examined [10].

However, no research exists on ZnO/WPU coatings for biodegradable PLA fabrics, especially in terms of UV transmittance and antibacterial features. This study focuses solely on the effect of ZnO concentration in WPU-based coatings on PLA fabric, in terms of UV transmittance and antibacterial properties. Coating formulations with four different ZnO concentrations, combined with a WPU binder, were applied to PLA spunlace NWFs using a film applicator and then thermally cured. Also, the prepared WPU/ZnO coating formulations were applied to glass plates as thin films and then

thermally cured. The synthesized ZnO particles obtained through a homogeneous phase reaction between zinc nitrate hexahydrate and sodium hydroxide were characterized by SEM and XRD. The chemical and thermal properties of thermally cured pure WPU and WPU/ZnO films were characterized by FTIR and DSC. The uniformity of ZnO distribution across the ZnO/WPU films and coated fabrics was examined by SEM.

2. Experimental

2.1. Materials

In this study, as a base material PLA spunlace fabric with fabric weight of 50 g/m^2 (Mogul Tekstil, Türkiye) was used. The list of materials used for preparing WPU/ZnO formulations was given in Table 1.

Table 1. Materials used in water-borne coating paste formulations

Materials	
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
Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, 98%,	Merck, Germany
Sodium hydroxide	Merck, Germany
Crosslinker	Trixene® Aqua BI 201, Lanxess, Germany
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	

2.2. Methods

2.2.1. Preparation and application of WPU/ZnO coatings on NWFs

WPU/ZnO composite formulations (Table 2) were created with varying ZnO concentrations, following methods from previous studies [8-10]. For ZnO nanopowder synthesis, zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) and NaOH (~20 wt.%) were used. First, 10 grams of $Zn(NO_3)_2 \cdot 6H_2O$ and 20 grams of NaOH were dissolved separately in 500 mL of deionized water. The NaOH solution was mixed with the $Zn(NO_3)_2$ solution and heated to 85°C, stirred at 750 rpm for 4 hours, then cooled.

The pH was adjusted to 7.5 using 20 wt% H_2SO_4, and the mixture was kept at 40°C for 2 hours before being filtered and rinsed with deionized water to collect the ZnO powder. ZnO, in the proportions specified in Table 2, was combined with 50 mL of deionized water. The ZnO dispersion and the blocked isocyanate crosslinker were then added to the binder-water mixture and mixed at 1500 rpm for 30 minutes using a mechanical stirrer (Weightlab WF-OD20). Following this, additives such as thickener, wetting agent, defoamer, and NH_4OH solution, as detailed in Table 2, were incorporated, and the mixture was stirred for an additional 30 minutes. The pH and viscosity measurements of coating pastes and applications on PLA nonwoven were made as described in previous studies [9, 10].

2.2.2. FTIR and SEM analysis

The thermally cured WPU/ZnO films underwent chemical analysis through FTIR spectroscopy (VERTEX 70v, Bruker, Germany), equipped with a universal ATR attachment and diamond crystal. The measurements were taken across a wavelength range of 400 to 4000 cm^{-1}, with a scan resolution of 4 cm^{-1}. SEM analysis was performed on ZnO powder, WPU-X, WPU/ZnO films, and fabric samples utilizing a FE-SEM instrument (Hitachi Regulus 8230) at an operating voltage of 10.0 kV. To enhance the electrical conductivity of the samples (both films and fabrics) before the analysis, a thin gold layer was applied to the surfaces using a Leica EM ACE600 coating system, with deposition rates between 0 to 10 nm/min.

2.2.3. DSC and XRD analysis

Thermal analysis of cured films was conducted using differential scanning calorimetry (DSC; Q20, TA Instruments). The device was set to heat from 25°C to 500°C at a rate of 10°C/min for both heating and cooling. The crystal structures and phases of ZnO powder were analyzed using XRD. The samples were ground to ~63 µm, dried at ~105±5°C for 4 hours, and then measured with an XRD device (Rigaku Miniflex 600) over a 2θ range of 5°-70°.

Table 2. Coating paste formulations

Formulation	DI Water (%)	WPU (%)	ZnO (%)	Crosslinker (%)	Thickener (%)	Wetting agent (%)	Defoamer (%)	NH_4OH solution (%)
WPU-X	18.61	75	0	2	2.63	0.75	0.46	0.55
WPU/ZnO-1%	18.61	75	1	2	2.63	0.75	0.46	0.55
WPU/ZnO-3%	18.61	75	3	2	2.63	0.75	0.46	0.55
WPU/ZnO-5%	18.61	75	5	2	2.63	0.75	0.46	0.55
WPU/ZnO-10%	18.61	75	10	2	2.63	0.75	0.46	0.55

2.2.4. UV-VIS measurements

Fabric samples (2 x 2 cm^2) were scanned over a wavelength range of 200 to 800 nm using a UV-VIS-NIR spectrometer (Shimadzu UV-3600 Plus) according to AATCC TM183 and UV protection levels were determined following ASTM D6603 [23].

2.2.5. Antibacterial activity

The antibacterial effectiveness of WPU/ZnO coated fabrics, influenced by different ZnO concentrations, was assessed against gram-positive and gram-negative bacteria. This test was made using the agar disc diffusion method, following the PN-EN ISO 20645:2006 standard for determining antibacterial activity in textile fabrics [24]. E. coli and S. aureus bacterial solutions with a density equivalent to the 0.5 McFarland standard were prepared. After spreading 100 µL of these bacterial solutions onto Mueller-Hinton agar, the coated fabrics were placed in the environment and incubated at 35 °C for 24 hours. The inhibition zone results formed after 24 hours were measured.

3. Results and Discussion

3.1. FTIR analysis results

The thermally cured pure WPU (WPU-X) film and WPU/ZnO composite coating films were analyzed by FTIR spectroscopy and composite films' FTIR spectra was given in Figure 1. FTIR spectra of the film prepared with WPU-X formulation showed the characteristic peaks of pure WPU [8-11].

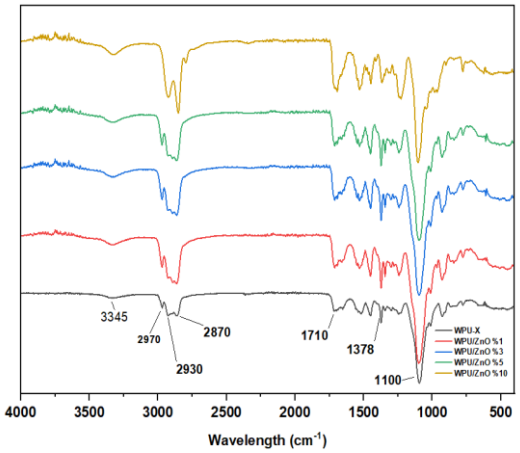

Figure 1. Fourier transform-infrared spectra of thermally cured films

The absorption peak observed at 3345 cm^{-1} was attributed to stretching vibrations caused by the -O-H- groups, and its intensity showed a notable increase with higher concentrations of ZnO. The absorption peaks at 2930 cm^{-1} and 2870 cm^{-1} were linked to asymmetric and symmetric $-CH_2$ groups. With the increase in ZnO concentration, the peak at the wavelength of 2930 was disappeared and the density of peaks occurred at 2970 cm^{-1} and 2870 cm^{-1} increased. The intensity of these peaks demonstrated an increase in correlation with higher concentrations of ZnO. The spectral bands ranging from 1460 to 1378 cm^{-1} reveal various modes of $-CH_3$ and $-CH_2$ vibrations. At the wavelength of 1100 cm^{-1}, the band is attributed to the deformation of O-C=O stretching vibration in the rigid urethane group, while at the wavelength of 778 cm^{-1}, the band is

associated with the out-of-plane bending of the ester group. The absorption band density observed at the wavelength of 1710 cm^{-1}, intensifying with higher ZnO concentration, was attributed to the presence of free and hydrogen-bonded –C=O groups [25].

The absorption peak in the C=O region exhibited an increase across all ZnO concentration levels. Nonetheless, the increase in absorption peaks for samples exceeding the amount of 5% ZnO showed a minor increment compared to those below 5%. The increase in the density of absorption peaks occurred at 3345 cm^{-1} implies that ZnO was incorporated into the PU matrix, thereby contributing to the disturbance of phase separation. The interaction between WPU and the surface hydroxyl groups on the ZnO particles emerged as the catalyst for disrupting the phase within the WPU matrix. The WPU/ZnO composite films exhibited a reduction in the formation of hard phases compared to the neat WPU film. This phenomenon arises from the interaction between WPU and the surface hydroxyl groups of ZnO-NPs, where each nanoparticle serves as a cross-linker, constraining the mobility of the polymer chains and consequently restricting and decreasing phase formation [26].

3.2. DSC analysis results

Thermal properties of WPU/ZnO films were investigated by DSC analysis. The results of DSC analysis results were given in Table 3. According to the results obtained, as the ZnO concentration increased in WPU/ZnO films, T_g and T_m values increased. WPU/ZnO films exhibited enhanced T_g and T_m values (T_g: 323.53 °C and T_m: 386.02 °C) compared to those of the WPU-X film analyzed in previous studies [8, 10]. The highest T_g and T_m values were obtained with the formulation including 10% ZnO nano powder. The rise in the Tg value due to decreased mobility of polymer chains, was attributed to a robust interaction between WPU polymer and ZnO particles [27].

Table 3. Thermal analysis results of composite films

Sample	T_g (°C)	$\triangle H_m$ (J/g)	T_m (°C)	$\triangle H_m$ (J/g)
WPU/ZnO 1%	343.51	30.57	412.63	56.57
WPU/ZnO 3%	344.71	48.22	413.51	65.08
WPU/ZnO 5%	348.43	48.50	414.09	63.05
WPU/ZnO 10%	371.42	110.0	452.74	65.73

3.3. XRD analysis results

XRD analysis was used to investigate the crystal structure of the synthesized ZnO nanopowder (Figure 2). The parameters of the synthesized ZnO, obtained from X-ray diffraction patterns, were provided in Table 4. The XRD patterns of the synthesized ZnO nanopowder closely obtained those of pure ZnO nanopowder [10]. Nine distinct peaks were observed at specific angles: 31.72, 34.37, 36.21, 48.07, 57.19, 63.61, 67.10, 68.72, and 69.85. These angles correspond to crystal planes of (100), (002), (101), (102), (110), (103), (200), (112), and (201). Notably, the intensity of the (101) peak is significantly higher than others, indicating it as the preferred growth plane for the samples. The average size of nanocrystalline (Table 4) was determined using the Debye-Scherrer formula [28].

Table 4. Parameters obtained from x-ray diffraction patterns

Sample	hkl	2Θ	Fwhm (deg)	Crystallite size (nm)
ZnO	100	31.88	0.371	22.2
ZnO	002	34.52	0.298	27.9
ZnO	101	36.36	0.411	20.3

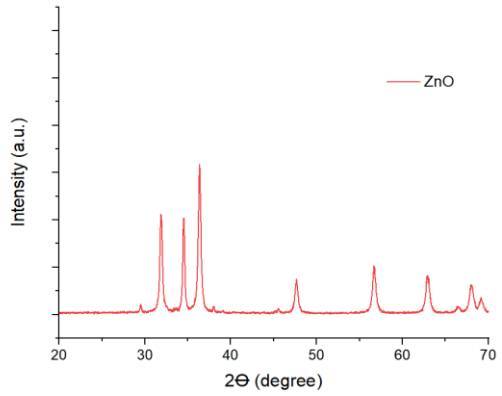

Figure 2. X-ray diffraction pattern of the synthesized ZnO nano powder

3.4. SEM analysis results

The analysis of the synthesized ZnO nano powder, WPU/ZnO composite film and coated PLA nonwoven fabric surface was performed by SEM (Figure 3). The presence of ZnO incorporated into the fabric structure was determined by SEM-EDX. The SEM analysis of composite film (Figure 3 (b)) showed that the ZnO particles (white regions) homogeneously distributed into the polymeric matrix including 10 wt.% of ZnO.

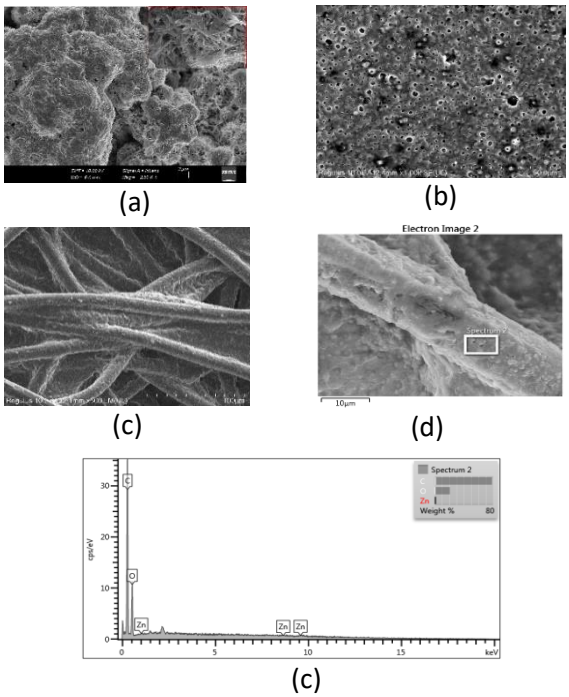

Figure 3. Scannig electron microscopy images of (a) zinc oxide nano powder, (b) thermally cured ZnO/WPU film (c) coated fabric surface (d) fiber surface image and (e) energy-dispersive x-ray spectrum of the coated fabric

It was observed that the WPU/ZnO coating paste coated on the fabric surface filled the gaps between the fibers of the fabric and the ZnO particles create a rough structure on the fiber surface. This indicated that the ZnO-NPs were evenly distributed in the WPU matrix and there is a good compatibility between them [24]. This aggregation may be attributed to the formation of interaction between ZnO particles and water molecules. SEM analysis demonstrated satisfactory filler homogeneity within the polymer matrix. However, notable agglomeration points were observed, particularly in regions with the high concentration of ZnO particles (Figure 3 (c) and Figure 3(d)) [25]. The presence of ZnO nanoparticles included in the fabric structure was confirmed by SEM EDX analysis (Figure 3 (e)).

3.5. UV-VIS measurement results

Table 5 presents the UV protection levels of coated fabrics, denoted by the transmittance values within the 200–800 nm wavelength range. The UV transmittance through the fabric plays a crucial role determining the UPF values of fabrics [28]. The UV transmittance values of the fabrics coated with WPU/ZnO coatings showed improvement compared to the uncoated PLA fabric and the PLA fabrics coated with ZnO-free coating paste (WPU-X), whose UV transmittance values were examined in previous studies [9, 10]. This reduction in UV trasmittance signifies enhanced UV blockage, preventing the UV rays from passing through the fabric surface [29]. The highest UPF value of 53.57 was obtained with the formulation of WPU/ZnO-10%. A higher UPF value indicates better protection against UV radiation [28].

3.6. Antibacterial activity results

In the antibacterial activity measurements, this analysis was performed using the agar disc diffusion method. After analysis, inhibition zones were measured, and the numerical results and photographic images were given in Table 6 and Figure 4, respectively.

Table 5. Ultraviolet protection factors and transmission values of coated NWFs

Sample	T(UVB) %	T(UVA) %	UPF	Blocking (UVA)	Blocking (UVB)	Protection Grade
WPU/ZnO-1%	18.52	20.22	5.14	79.78	81.48	-
WPU/ZnO-3%	8.41	10.03	8.28	89.97	91.59	-
WPU/ZnO-5%	4.49	7.56	20.80	92.44	95.51	Good
WPU/ZnO-10%	3.96	7.11	53.57	92.89	96.04	Very Good

It was determined that the fabrics coated with formulations containing 1% and 3% ZnO have no antibacterial activity against E. coli and S. aureus bacteria. While the fabric coated with the formulation containing 5% ZnO has no resistance to E. coli, resistance was obtained against S. aureus bacteria. The diameter of the inhibition zone was measured as 17.75 ± 0.35 mm. Inhibition zone diameters against E. coli and S. aureus bacteria were measured as 15.5 ± 0.70 mm and 18.25 ± 0.35 mm, respectively in the fabric coated with the formulation including 10 % ZnO. Due to bacterial attack degradation of various polymer materials poses a common issue.

Table 6. Inhibition zone measurements of coated fabrics against to bacteria

Sample	E. coli (ATCC 25922) inhibition zone (mm)	S. aureus (ATCC 25923) inhibition zone (mm)
Uncoated fabric	-	-
WPU/ZnO %1	-	-
WPU/ZnO %3	-	-
WPU/ZnO %5	-	17.75 ± 0.35
WPU/ZnO %10	15.5 ± 0.70	18.25 ± 0.35
Positive control streptomycin	19	21

When exposed to suitable environment, bacteria can proliferate on the material's surface, rendering it significantly compromised for use. Addressing this issue involves employing various strategies to shield the material from bacterial attacks. A particularly effective approach is augmenting antibacterial capabilities through the incorporation of metal oxide nanoparticles, specifically tailored for the material. Utilizing ZnO in PU/ZnO nanocomposites has proven beneficial in enhancing antibacterial properties. Typically, pristine PU materials exhibit negligible antibacterial properties. However, the incorporation of ZnO into the PU matrix leads to a substantial enhancement of antibacterial attributes [30].

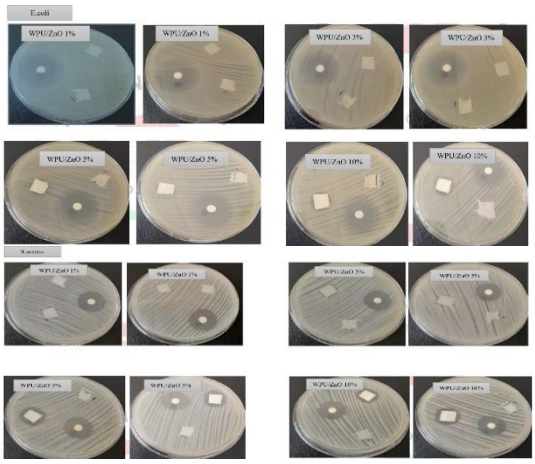

Figure 4. Antibacterial activities of uncoated and coated spunlace fabrics against bacteria

Smaller ZnO nanoparticles can penetrate bacterial membranes due to their large surface area, enhancing their antibacterial effectiveness. A significant difference in antibacterial activity was observed between S. aureus and E. coli, with S. aureus showing better susceptibility. The antibacterial efficacy increased with higher concentrations of ZnO NPs, as shown in Figure 4, which depicts a larger inhibition zone for both E. coli and S. aureus with higher ZnO NP concentrations. The antimicrobial effects of ZnO NPs are primarily due to their disruption of bacterial and fungal cell membranes, likely through the generation of reactive oxygen species such as superoxide anions, hydroxyl radicals, and hydroxyl ions [26].

4. Conclusion

In this study, ZnO nanoparticles were synthesized using wet chemical methods. WPU/ZnO composite coatings were prepared and applied to PLA spunlace NWFs using a film applicator. The functional properties of the coated and thermally cured fabrics were assessed for UV protection and antibacterial activity. FTIR analysis revealed that increasing ZnO concentration enhanced the absorption peaks

related to C=O groups in the WPU/ZnO composite films. XRD analysis confirmed the successful synthesis of ZnO nanopowder by verifying its crystal structure. In the SEM analysis, surface analyzes of coated and cured films and fabrics showed that ZnO-NPs were evenly distributed in the WPU matrix and there was good compatibility between them. DSC analysis of cured composite films showed that with the increase in ZnO concentration a decrease occurred in the mobility of polymer chains due to a strong interaction between WPU polymer and ZnO particles and T_g and T_m values improved.

Higher UV protection properties were obtained with the fabrics coated with the formulation including having higher ZnO concentration. The highest UPF value of 53.57 was obtained with the fabric coated with the formulation of WPU/ZnO-10%. This result was attributed to UV absorption properties of ZnO nanoparticles. In the antibacterial activity analysis, the more effective antibacterial activity was obtained with the fabric coated with the WPU/ZnO 10% formulation having higher ZnO concentration. The results of this study revealed that biodegradable sustainable functional NWFs with UV protection effect and antibacterial activity can be develop with composite coatings including WPU and ZnO nanoparticles.

The findings demonstrated that employing binders to immobilize nanoparticles within NWF structures could offer a promising pathway for creating highly efficient antibacterial materials, paving the way for future applications. The primary advantages of utilizing WPU/ZnO composite materials lie in their biocompatibility and potential antibacterial properties, making them highly suitable for both medical applications and particularly for their UV protection attributes they may be suitable for everyday use. The main uses of PLA NWFs coated with WPU/ZnO composite coatings may be medical textiles applications such as hospital bedding, gloves, surgical drapes.

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Authors' Contribution
The author is responsible for the design, implementation, analysis of the results, and writing of this study.

The Declaration of Conflict of Interest/ Common Interest
No conflict of interest or common interest has been declared by the author.

The Declaration of Ethics Committee Approval
This study does not require ethics committee permission or any special permission.

The Declaration of Research and Publication Ethics
The author of the paper declare that they comply with the scientific, ethical and quotation rules of SAUJS in all processes of the paper and that she does not make any falsification on the data collected. In addition, she declares that Sakarya University Journal of Science and its editorial board have no responsibility for any ethical violations that may be encountered, and that this study has not been evaluated in any academic publication environment other than Sakarya University Journal of Science.

References

[1] E. O. Ogunsona, R. Muthuraj, E. Ojogbo, O. Valerio, T. H. Mekonnen, "Engineered nanomaterials for antimicrobial applications: A review," Applied Materials Today, vol. 18, p. 100473, 2020.

[2] I. S. Tania, M. Ali, M. Akter, "Fabrication, characterization, and utilization of ZnO nanoparticles for stain release, bacterial resistance, and UV protection on cotton fabric," Journal of Engineered Fibers and Fabrics, vol. 17, 2022.

[3] S. Kathirvelu, L. D'Souza, B. Dhurai, "UV protection finishing of textiles using ZnO nanoparticles," Indian Journal of Fibre & Textile Research, vol. 34, no. 3, pp. 267–273, 2009.

[4] A. Verbič, M. Gorjanc, B. Simončič, "Zinc oxide for functional textile coatings: Recent advances," Coatings, vol. 9, no. 9, pp. 17–23, 2019.

[5] G. Zhang, Y. Liu, H. Morikawa, Y. Chen, "Application of ZnO nanoparticles to enhance the antimicrobial activity and ultraviolet protective property of bamboo pulp fabric," Cellulose, vol. 20, no. 4, pp. 1877–1884, 2013.

[6] P. Sikdar, S. Islam, A. Dhar, G. Bhat, D. Hinchliffe, B. Condon, "Barrier and mechanical properties of water-based polyurethane-coated hydroentangled cotton nonwovens," Journal of Coatings Technology and Research, vol. 19, no. 4, pp. 1255–1267, 2022.

[7] Y. Zhang, T.-T. Li, C.-W. Lou, J.-H. Lin, "Facile method for tent fabrics with eco-friendly/durable properties using waterborne polyurethane/lignin: Preparation and evaluation," Journal of Industrial Textiles, vol. 51, no. 3, pp. 4149S-4166S, Jun. 2022.

[8] G. Baysal, "Investigation of barrier effectiveness and comfort properties of biodegradable PLA nonwoven fabrics coated with unmodified lignin/water-borne polyurethane composite coatings," Hittite Journal of Science and Engineering, vol. 11, no. 2, pp. 77–88, Jun. 2024.

[9] G. Baysal, "Mechanical and UV protection performances of polylactic acid spunlace nonwoven fabrics coated by eco-friendly lignin/water-borne polyurethane composite coatings," Journal of The Textile Institute, vol. 0, no. 0, pp. 1–13, 2023.

[10] G. Baysal, "Sustainable polylactic acid spunlace nonwoven fabrics with lignin/zinc oxide/water-based polyurethane composite coatings," International Journal of Biological Macromolecules, vol. 254, no. P1, p. 127678, 2024.

[11] G. Baysal, "Effect of lignin / water-borne polyurethane composite coatings on tensile strength and UV protection properties of PET/PA6 bicomponent nonwoven fabrics," Pamukkale University Journal of Engineering Sciences, 2024.

[12] X. Liu, D. Jiang, Y. Qin, Z. Zhang, M. Yuan, "ZnO-PLLA/PLLA preparation and application in air filtration by electrospinning technology," Polymers (Basel)., vol. 15, no. 8, pp. 1–12, 2023.

[13] A. Y. Nikiforov, X. Deng, I. Onyshchenko, D. Vujosevic, V. Vuksanovic, U. Cvelbar, N. De Geyter, R. Morent, C. Leys, "Atmospheric pressure plasma deposition of antimicrobial coatings on non-woven textiles," The European Physical Journal Applied Physics, vol. 75, no. 2, pp. 1–6, 2016.

[14] P. Ramamurthy, K. P. Chellamani, B. Dhurai, S. P. Thankarajan, B. Subramanian, E. Santhini, "Antimicrobial characteristics of pulsed laser deposited metal oxides on polypropylene hydroentangled nonwovens for medical textiles," Fibres & Textiles in Eastern Europe, vol. 25, no. 2, pp. 112–119, 2017.

[15] Y. Dong, N. L. Thomas, X. Lu, "Electrospun dual-layer mats with covalently bonded ZnO nanoparticles for moisture wicking and antibacterial textiles," Materials & Design., vol. 134, pp. 54–63, 2017.

[16] T. Ferreira, A. C. Vale, A. C. Pinto, R. V. Costa, V. Pais, D. Sousa, F. Gomez, G. Pinto, J. G. Dias, I. P. Moreira, C. Mota, J. Bessa, J. C. Antunes, M. Henriques, F. Cunha, R. Fangueiro, "Comparison of zinc oxide nanoparticle integration into non-woven fabrics using different functionalisation methods for prospective application as active facemasks," Polymers (Basel)., vol. 15, no. 17, pp. 1–21, 2023.

[17] I. S. Tania, M. Ali, "Effect of the coating of zinc oxide (ZnO) nanoparticles with binder on the functional and mechanical properties of cotton fabric," Materials Today: Proceedings, vol. 38, pp. 2607–2611, 2020.

[18] G. Zhang, Y. Xiao, J. Yan, W. Zhang, "Fabrication of ZnO nanoparticle-coated calcium alginate nonwoven fabric by ion exchange method based on amino hyperbranched polymer," Materials Letters, vol. 270, no. 3, p. 127624, 2020.

[19] B. Deng, Q. Wei, W. Gao, "Physical properties of Al-doped ZnO films deposited on nonwoven substrates by radio frequence magnetron sputtering," Journal of Coatings Technology and Research, vol. 5, no. 3, pp. 393–397, 2008.

[20] G. Deshmukh, "ZnO coated nonwoven polypropylene fabric with antibacterial and antiviral function for medical applications," 2022 International Conference on Emerging Trends in Engineering and Medical Sciences ICETEMS 2022, pp. 395–400, 2022.

[21] Ş. S. Uğur, M. Sariişik, A. H. Aktaş, M. Ç. Uçar, E. Erden, "Modifying of cotton fabric surface with Nano-ZnO multilayer films by Layer-by-Layer deposition method," Nanoscale Research Letters, vol. 5, no. 7, pp. 1204–1210, 2010.

[22] R. Zhang, L. Tang, X. Ji, Y. Su, N. Xu, Y. Feng, L. Pan, "Continuous preparation and antibacterial mechanisms of biodegradable polylactic acid/nano-zinc oxide/additives antibacterial non-wovens," International Journal of Biological Macromolecules, vol. 269, Part 2, 132188, Jan. 2024.

[23] K. A. V. Prilla, J. M. Jacinto, L. J. O. Ricardo, J. T. S. Box, A. B. C. Lim, E. F. Francisco, G. I. N. De Vera, J. A. T. Yaya, V. V. M. Natividad, E. N. Awi, R. Encina, "Flame retardant and UV-protective cotton fabrics functionalized with copper (II) oxide nanoparticles," Antorcha, vol. 7, no. 2, pp. 11–16, 2021.

[24] M. H. Kudzin, Z. Mrozińska, "Biofunctionalization of textile materials. 2. antimicrobial modification of poly(lactide) (PLA) nonwoven fabrics by fosfomycin," Polymers (Basel)., vol. 12, no. 4, p. 768, Apr. 2020.

[25] S. Vlad, C. Ciobanu, R. V Gradinaru, L. M. Gradinaru, A. Nistor, "Antibacterial evaluation of some polyurethane membranes modified by zinc oxide nanoparticles," Digest Journal of Nanomaterials and Biostructures, vol. 6, no. 3, pp. 921–930, 2011.

[26] T. S. Velayutham, W. H. Abd Majid, W. C. Gan, A. Khorsand Zak, S. N. Gan, "Theoretical and experimental approach on dielectric properties of ZnO nanoparticles and polyurethane/ZnO nanocomposites," Journal of Applied Physics, vol. 112, no. 5, 2012.

[27] R. R. Soares, C. Carone, S. Einloft, R. Ligabue, W. F. Monteiro, "Synthesis and characterization of waterborne polyurethane/ZnO composites," *Polymer Bulletin*, vol. 71, no. 4, pp. 829–838, 2014.

[28] A. Belay, M. Mekuria, G. Adam, "Incorporation of zinc oxide nanoparticles in cotton textiles for ultraviolet light

protection and antibacterial activities," Nanomaterials and Nanotechnology, vol. 10, pp. 1–8, 2020.

[29] I. S. Tania, M. Ali, M. Akter, "Fabrication, characterization, and utilization of ZnO nanoparticles for stain release, bacterial resistance, and UV protection on cotton fabric," Journal of Engineered Fibers and Fabric, vol. 17, pp. 1–11, Jan. 2022.

[30] M. M. Rahman, "Polyurethane/zinc oxide (PU/ZnO) composite-synthesis, protective property and application," Polymers (Basel)., vol. 12, no. 7, 2020.