

Pasupathy Ramamurthy^{1*},
Kandan Perumal Chellamani¹,
Bharaathi Dhurai²,
Senthil Perumal ThankaRajan³,
Balasubramanian Subramanian³,
Elango Santhini⁴

Antimicrobial Characteristics of Pulsed Laser Deposited Metal Oxides on Polypropylene Hydroentangled Nonwovens for Medical Textiles

DOI: 10.5604/12303666.1228192

¹The South India Textile Research Association,
Coimbatore, India
*Email: ramamurthypasupathy@rediffmail.com

²Department of Textile Technology,
Kumaraguru College of Technology,
Coimbatore, India

³Central Electrochemical Research Institute,
Karaikudi, India

⁴COE Medical Textiles,
The South India Textile Research Association,
Coimbatore, India

Abstract

In this study, an attempt was made to investigate the antimicrobial activity on polypropylene (PP) hydroentangled nonwoven fabrics coated with transition metal oxides. After etching the nonwoven fabrics with RF plasma, nano-scale coatings of ZnO and CuO were done using the KrF excimer based pulsed laser deposition technique (PLD). Morphological and antimicrobial studies were carried out to elucidate the mechanism of antibiocide behaviour of the coated fabrics. Results showed significant antibacterial activity of ZnO and CuO coated PP hydroentangled nonwovens with a better activity against gram positive S.aureus than gram negative E.coli. Inherently non-toxic, PP has excellent chemical resistance and the use of specialised PP fibres for hydroentangled nonwovens could offer scope in addition to metal oxide coatings; nano-scale biological materials such as enzymes and drugs could add specific functionality for their use as medical textiles.

Key words: antibacterial activity, metal oxides, pulsed laser deposition, energy dispersive X-ray (EDX), polypropylene, hydroentangled nonwoven.

Introduction

Olefin polymers such as polypropylene (PP) have been widely used in medical textiles due to their unique characteristics such as superior chemical resistance and good mechanical properties, as well as the nominal costs. These make them suitable in single use health care and hygiene products, medical textiles, etc. The antimicrobial function of polymeric materials can be attained by physical or chemical incorporation of biocides into polymer substrates [1].

Generally PP based nonwovens are found to be hydrophobic and it is necessary to improve their hydrophilicity to widen their applicability for medical use. The use of gas plasma has led to the surface modification of substrate material and has enhanced its functional characteristics [2]. Plasma treatment can be used for surface activation and has wide textile applications.

Functional finishing of textiles using nanoparticles has been studied by many researchers with a view to enhancing their antimicrobial and self-cleaning properties [3]. The use of conventional methods for the functional finishing of textiles caused undesirable effects like the weight of add-ons, loss of comfort characteristics, decrease in material strength and durability aspects. Different techniques are available for nano particle coating on textile materials that include enzyme immobilisation; in which various methods like adsorption, covalent bonding, encapsulation, entrapment, enzyme crosslinking, etc. are commercially adopted.

The use of metals as biocides, in particular nano structured gold and silver deposited on PP nonwovens has been studied widely to evaluate the antibacterial properties by many researchers [4-9]. Metal oxides and their compounds of very low concentrations were also found to be toxic to microbes [10, 11]. The mechanism of action for the destruction of the bacteria was found to be varied, including binding to cellular proteins, which causes inactivation, the generation of reactive oxygen species and direct cell wall damage. Most of the commonly used metal oxides studied were ZnO, CuO, MgO, TiO₂ and AgO.

Various techniques available for the nano coating of metal biocides include the use of nanosols, polymer dispersion of nano-sized metal oxides like silver, TiO₂,

ZnO, aluminium, silica, etc. [12-14], chemical vapour deposition (CVD) involving the deposition of a solid material film from a gaseous phase [15, 16], physical vapour deposition (PVD), where the material to be deposited is taken as a solid substrate and vaporised to be deposited on the intended target fabric [17], atomic layer deposition (ALD) [18] and plasma coating for special end uses. Metal oxide coatings at the nano-level present a larger surface area for greater interaction with increased durability and selective toxicity to microorganisms along with safety and non-toxicity to humans [19-26].

The use of other metal oxides like copper oxides (CuO), zinc oxides (ZnO), etc. with different techniques of deposition was studied for polyolefin spun bonded fabrics [27] and found to destroy microorganisms, besides being safe to humans. Nano composite fibres for permanent bacteriostatic application on textile and medical applications are being researched [28]. Yamamoto et al, observed that the antibacterial activities of nanoparticles are positively correlated with the size, which means an increase in the surface area with a smaller size for better results [29].

In this study, an attempt was made to investigate the antimicrobial activity of coated hydroentangled PP nonwovens with the KrF excimer based pulsed laser deposition of metal oxides like CuO, ZnO and ZnO/CuO.

Experimental

Materials

Hydroentangled nonwoven polypropylene (PP) fabrics of 100 gsm (F1), 150 gsm (F2) produced from 1.7 dtex fibres was prepared on a Rieter Perfo-jet hydro entangle nonwoven plant (France) using standard production parameters. The PP fibres (HY-Entangle HOP Phil, Fiber Visions a/s, Denmark) used for the fabric preparation are specially meant for hydroentangled nonwoven manufacture whose typical fibre properties are given in **Table 1**. For comparative purposes a needle punched nonwoven web from the same PP fibre with a fabric weight of 150 gsm (Fo) was prepared on a Dilo needle punching nonwoven line (Germany). An 8 ply cotton woven gauze mopping pad (Fc) was also used as a candidate for the coating of metal oxides and used as a control material.

Methods

Coating of metal oxide-sample preparation

Nonwoven PP fabrics and cotton gauze samples were treated with acetone to remove the spin finishes or other additives used during their manufacture. After washing the material using de-ionised water, the swatches were dried at 60°C prior to cutting into 2 x 2 inch specimens for coating by pulsed laser deposition after plasma etching.

Plasma treatment

The PP nonwoven and cotton swatches were subjected to plasma treatment using argon gas under the following conditions: pressure of 0.44 millibar, temperature of 29°C, plasma voltage of 300 V, current of 0.65 A and a time of 5 mins each for the front and reverse sides of the fabric. The equipment used was a Plasma System Model HPVT_PS (Hydro Pneo VAC technologies, India).

Pulsed laser deposition of metal oxides

After argon plasma etching of the PP nonwovens to increase the adhesion of the coatings, the samples of 2 x 2 inch dimensions was coated with CuO, ZnO, and ZnO/CuO multi-layer using the pulsed laser deposition technique.

ZnO and CuO coating was deposited on fabrics using a KrF gas excimer (Coherent compex pro) by means of a Laser Ablation Vacuum Coating unit (Hind High Vacuum Co. P. Ltd, India). Commercial ZnO and the copper targets were loaded

on to the target holder and the substrate (fabric) was clamped on the substrate holder. The target used for coating was 99.9% pure ZnO and Cu, sourced from Alfa Aesar, India. Reactive pulsed laser ablation was done in an oxygen atmosphere, and the deposition with optimised deposition parameters and conditions, detailed in **Table 2**.

Morphological characterisation of the coated fabrics

Surface morphology on SEM

A Carl Zeiss FESEM Zigma VP (Germany) scanning electron microscope was used to study the surface morphology of the coated samples. Suitable magnifications were used to reveal the form of coatings on the reference materials. Analysis of the coatings identified the presence of metal oxides adhering to the surface of the fibres.

XRD

The structure of the coatings and the impregnation of nanoparticles into the fabrics were examined using a Bruker D8 Advance X-ray diffractometer (USA) operating in the Bragg-Brentano mode.

An energy dispersive X-Ray (EDX) from Oxford Instruments, UK, was used to analyse the surface elemental compositions with their respective weightings. XRD analysis was also done to characterise the ZnO and CuO nano particles coated on the PP nonwoven fabrics. The diffracted intensities were analysed from 30 to 80°2θ angles.

Pore size distribution

In order to estimate the permeability characteristics of the plasma treated and ZnO/CuO coated PP nonwoven fabrics, a capillary flow porometer (ACFP-1020A) from M/s Porous Materials, Inc., USA, was used. Capillary flow porometry, also known as porometry, is a characterisation technique based on the displacement of a wetting liquid from the sample pores by applying a gas at increasing pressure [30]. It is widely used to measure minimum, maximum (bubble point) and mean flow pore sizes, as well as pore size distribution of the through pores in membranes nonwovens, paper, filtration and ultrafiltration media, hollow fibres, ceramics, etc.

In capillary flow porometry, a wetting liquid is allowed to spontaneously fill the pores in the fabric sample and a non-reacting gas is allowed to displace liquid

Table 1. Fibre properties of polypropylene HY entangle.

Fibre type	Polypropylene HY entangle
Fineness	1.7 dtex
Tensile strength	2.3-3.5 cN/dtex
Elongation	100-300%
Fibre length	40 mm
Shrinkage	3-8%
Spin finish level	0.35%

Table 2. Optimised parameters and conditions of the pulsed laser deposition process.

Laser	KrF excimer (248 nm)
Repetition rate	20 Hz
Pulse duration	9 ns
Pulse energy	400 mJ/pulse
Target	ZnO, Cu
Substrate	PP nonwoven fabrics
Deposition temperature	Room temperature – 36°C
Atmosphere	Oxygen
Base vacuum	3 × 10 ⁻⁶ mbar
Oxygen pressure	1.3 × 10 ⁻³ mbar

from the pores. The gas pressure and flow rates through wet and dry samples are being accurately measured. The gas pressure required for removing liquid from the pores causing gas to flow is given by:

$$D = 4 \gamma \cos \theta / P \quad (1)$$

Where D is the pore diameter, γ is the surface tension of the liquid, θ is the contact angle of the liquid, and P is the differential pressure of the gas.

From the gas pressure and flow rates measured, the pore throat diameters and pores size distribution are calculated.

Antibacterial activity assessment

The term 'antimicrobial activity' refers to a material that destroys, inhibits or prevents the propagation, growth and multiplication of microbial organisms. In the present study, the relative antibacterial activity of ZnO and CuO coated fabrics were studied against *E.coli* and *S.aureus* qualitatively by the disk diffusion Kirby-Bauer method as per standard protocols [31]. The organisms were briefly swabbed in the Muller-Hinton agar plates, and fabric disks of 10 mm diameter of the control (uncoated) and the antimicrobial coated (ZnO, CuO and multi-layer ZnO/CuO) were then gently pressed on to the surface of the plates.

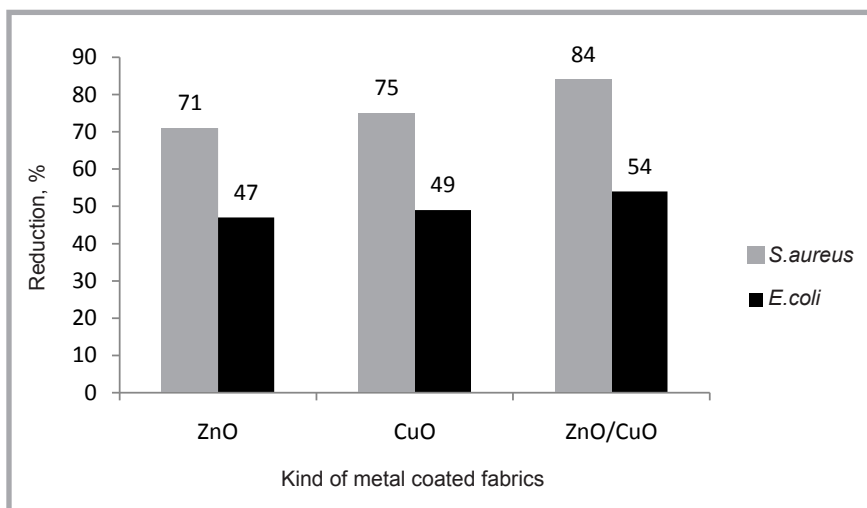


Figure 1. Antibacterial efficiency of metal coated PP nonwoven fabrics against different bacteria using absorption method.

Table 3. Antibacterial activity of metal oxide coated PP fabrics using absorption method. Note: B2-Untreated hydroentangled fabric F1, Z2- ZnO coated hydroentangled nonwoven fabric F1. C2 – CuO coated hydroentangled nonwoven fabric F1, ZC2 – ZnO/CuO coated hydroentangled fabric F1.

Sample ID	Absorbance at 625 nm		Reduction, %	
	<i>S. aureus</i>	<i>E. coli</i>	<i>S. aureus</i>	<i>E. coli</i>
Untreated PP hydroentangled nonwoven fabric (B2)	0.56	0.56	0	0
ZnO coated PP hydroentangled nonwoven fabric (Z2)	0.16	0.16	71	53
CuO coated PP hydroentangled nonwoven fabric (C2)	0.14	0.14	75	51
ZnO/CuO coated PP hydroentangled nonwoven fabric (ZC2)	0.09	0.09	84	96.4

The plates were incubated for 24 hrs. at 37°C. Presence of antimicrobial activity was identified by analysing the zones around the fabric disks.

The antibacterial effect was also investigated quantitatively for these coated samples using the Shake Flask Test in accordance with ASTM E2149-13 [32]. In this method, coated test samples are placed in a laboratory flask containing a dilute suspension of the test organism. Here the test bacteria certified for testing purposes used were *E. coli* (AATCC 8739) and *S. aureus* (AATCC 25923). The flasks were shaken vigorously for 1 hour. Following exposure, a sample of the test organism suspension was removed and quantitatively assayed for survivors. Afterwards the plates were incubated at 37 ± 1°C for 24 hrs and the number of survivors were enumerated and the percentage reduction determined for the test flask as compared to the untreated control suspension (control

uncoated material) using the following formula:

$$R_s = \frac{X-Y}{X} \times 100 \quad (2)$$

Where,

- R_s – reduction percentage of bacteria
- X – number of bacterial colonies recovered from the bacterial solution at '0' contact time
- Y – number of bacterial colonies recovered from the specimen after shaking for 1 hr.

If the number of bacteria after shaking is larger than that at '0' contact time, then $R_s = 0$.

To elucidate the mechanism of antibacterial activity of ZnO, CuO and ZnO/CuO coated fabrics, bacterial cultures *S. aureus* and *E. coli* at concentrations of 10^8 CFU/ml were grown on the untreated and coated fabrics for 24 hrs. at 37°C. After incubation, the fabrics were gently washed with 1X PBS (pH – 7.2), dehydrated with dif-

ferent concentrations of ethanol (10% to 100%), and freeze dried overnight.

The resultant cultures were measured spectrophotometrically as per the modified ISO 20743:2007 and analysed for antibacterial activity as follows:

$$1 - \left(\frac{OD_{625} \text{ coated fabric}}{OD_{625} \text{ untreated fabric}} \right) \times 100 \quad (3)$$

Where, OD_{625} of the coated fabric is the optical density at 625nm of metal (ZnO, CuO & ZnO/CuO) coated PP Hydroentangled nonwoven fabric, and OD_{625} of the untreated fabric is the optical density of metal untreated PP hydroentangled nonwoven fabric (control).

Results and discussion

Antibacterial performance

The antibacterial activity of ZnO, CuO and ZnO/CuO coated fabrics was assessed using four different methods viz., the disc diffusion, parallel streak, absorption and shake flask methods in order to investigate the antibacterial efficacy under different conditions. The antibacterial activity of textile materials to inhibit bacterial growth was first tested using the disc diffusion method against *S. aureus* (ATCC 6538) and *E. coli* (ATCC 25922). The zone of inhibition was not observed against the test organisms for all the fabric candidates, suggesting that the coatings carried out by the PLD technique using ZnO and CuO are non-diffusible, hence they did not diffuse into the agar medium to produce the halo effect for both types of bacteria studied.

The antibacterial efficacy of the metallic oxide coated fabric was determined using the absorption method with nutrient broth as the medium. The bacterial growth when in direct contact with the metal oxide coated fabric was monitored after 24 h incubation by measuring the optical density of the medium. The percentage of microbial reduction with the metallic oxide coated fabric against both species of bacteria is shown in **Table 3**. In **Figure 1** graphs are included showing the change in absorbance after 24 h of incubation. A high antimicrobial activity was seen against Gram positive bacteria i.e., 84% reduction in growth for *S. aureus* with ZnO/CuO, followed by CuO (75%) and ZnO (71%), as shown in **Table 3**. However, the activity was minimal against Gram negative organisms.

Absorbance measurements are not as accurate as plate counts for the determination of viable bacteria, but they can give a rapid estimate of cell numbers. Absorbance measurements (turbidity) are commonly used for minimum inhibitory concentration (MIC) and minimum bactericidal concentration (MBC) tests [33].

Hence the dynamic shake flask method was performed as per ASTM E 2149-13 for routine quality control and screening tests in order to overcome difficulties in using conventional antimicrobial test methods such as ensuring proper contact of inoculums to the surface treated. This variant of the shake flask method is quicker to perform and gives an indication of bacterial efficiency within 24 hours, whereas it takes at least 3 days to get the results by conventional plating methods. **Table 4** gives the results of antibacterial assessments of PP nonwovens (needle punched and hydroentangled fabrics) besides a cotton gauze pad for *S.aureus* and *E.coli* bacteria.

Table 4 gives the results of antibacterial assessments of PP nonwovens (needle punched and hydroentangled fabrics) besides cotton gauze fabric for *S.aureus* and *E.coli* bacteria.

CuO, ZnO and ZnO/CuO coated PP nonwovens and the cotton gauze pad were more effective against *S.aureus*, exhibiting a 100% inhibition for all the reference fabrics. However, the inhibition rates for *E.coli* were not much as compared to *S.aureus*. The coated cotton gauze pad showed a 100% inhibition for both test bacteria. One possible reason for the variations between the microorganisms for the same level of metal oxide coating may be the differences in the cell wall configuration and the peptidoglycon and lipopolysaccharide constituents in the bacterial structure studied. Another aspect that needs to be considered and has been reported in literature [4-9] is bacterial inhibition, which is dependent on the total amount of metal constituents released from the coatings, which means to say that increasing the surface area of the coatings would obviously better the antibacterial performance.

Metals like silver, zinc, copper, etc. have been traditionally recognised to have antibacterial properties and have been used for many therapeutic treatments. However, metal oxides like ZnO, CuO have been studied for their use as inorganic bioc-

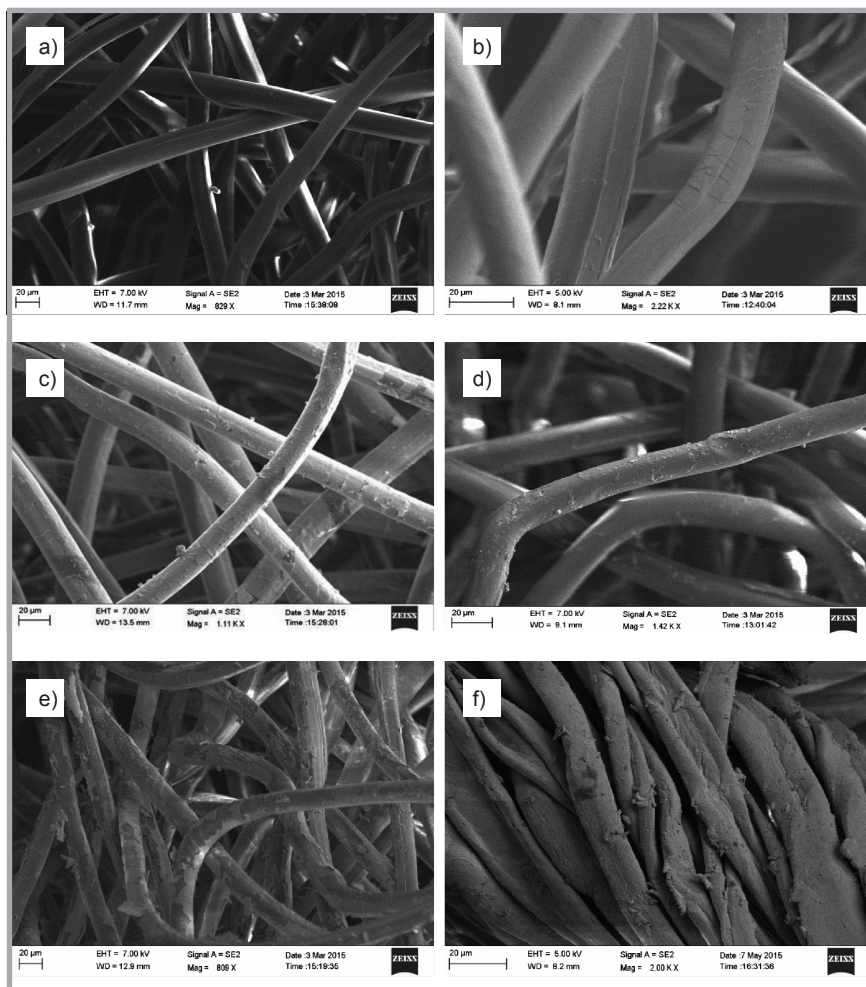


Figure 2. SEM images of coated fabrics (a) uncoated PP nonwoven; (b) plasma treated PP nonwoven; (c) ZnO coated PP nonwoven; (d) CuO coated PP nonwoven; (e) ZnO + CuO coated PP nonwoven; (f) ZnO + CuO coated woven cotton gauze fabric.

Table 4. Antimicrobial assessment of coated fabrics. Medium used: nutrient agar. Test: Shake Flask Test ASTM E2149-13. **Note:** Fo-needle punched PP nonwoven fabric, F1-hydroentangled PP nonwoven fabric 100 gsm, F2-hydroentangled PP nonwoven fabric 150 gsm, Fc-cotton woven gauze fabric.

S.No.	Sample ID	Sample details	Rs (% of inhibition)	
			<i>S. aureus</i>	<i>E. coli</i>
1.	Z1	ZnO coated needle punched PP nonwoven fabric Fo	100	5.25
2.	Z2	ZnO coated hydroentangled PP nonwoven fabric F1	100	6.10
3.	Z3	ZnO coated hydroentangled PP nonwoven fabric F2	100	15.50
4.	Z4	ZnO coated cotton woven gauze fabric Fc	100	100
5.	ZC1	ZnO/CuO coated needle punched PP nonwoven fabric Fo	100	2.50
6.	ZC2	ZnO/CuO coated hydroentangled PP nonwoven fabric F1	100	5.85
7.	ZC3	ZnO/CuO coated hydroentangled PP nonwoven fabric F2	100	25.25
8.	ZC4	ZnO/CuO coated cotton woven gauze fabric Fc	100	100
9.	C1	CuO coated needle punched PP nonwoven fabric Fo	100	10.50
10.	C2	CuO coated hydroentangled PP nonwoven fabric F1	100	22.00
11.	C3	CuO coated hydroentangled PP nonwoven fabric F2	100	42.85
12.	C4	CuO coated cotton woven gauze fabric Fc	100	99.00
13.	B1	Untreated needle punched PP nonwoven fabric Fo	0	0
14.	B2	Untreated hydroentangled PP nonwoven fabric F1	0	0
15.	B3	Untreated hydroentangled PP nonwoven fabric F2	0	0
16.	B4	Untreated cotton woven gauze fabric Fc	0	0

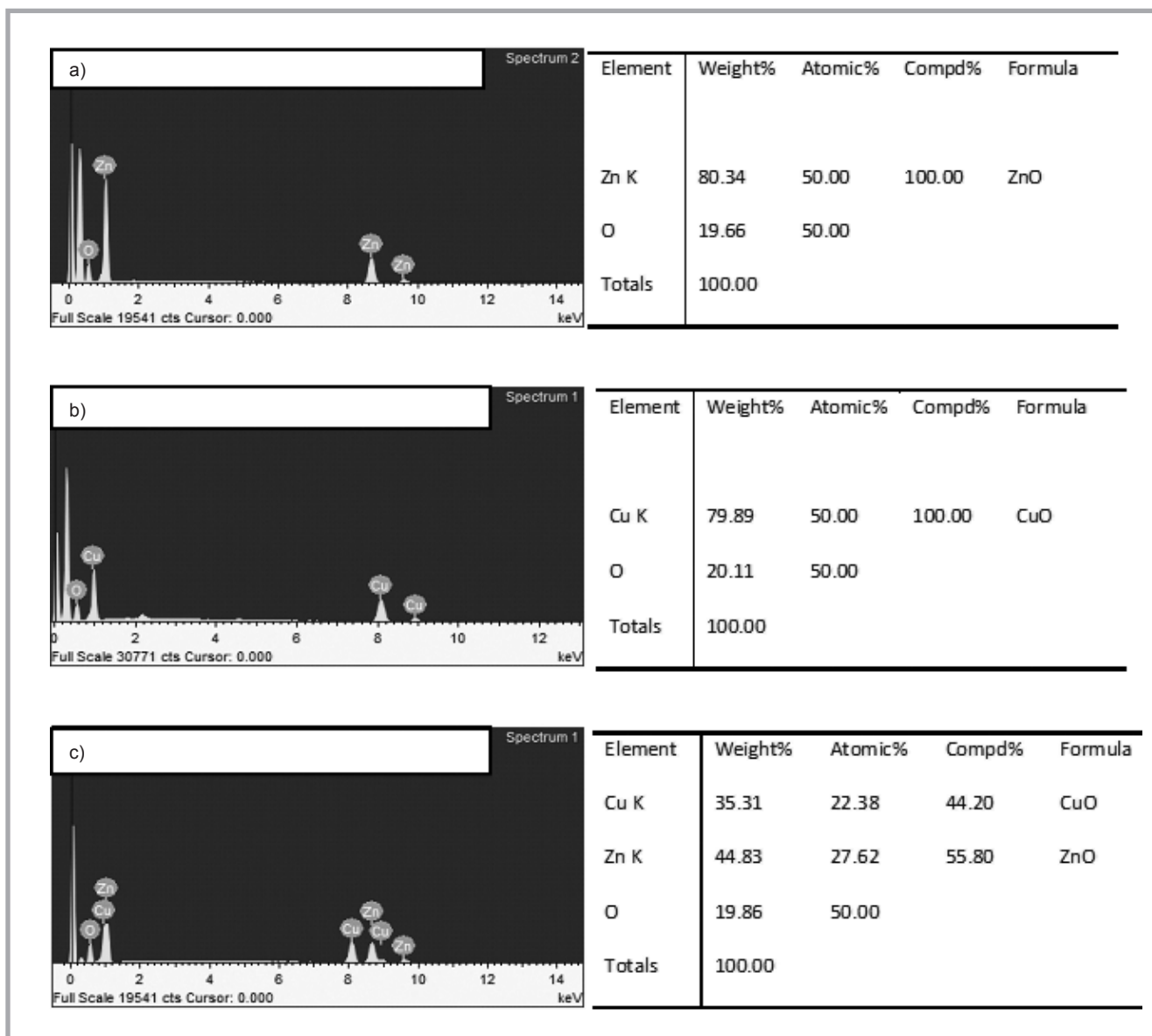


Figure 3. EDX spectra and elemental compositions of coated fabrics (a) ZnO coated PP nonwoven fabric, (b) CuO coated PP nonwoven fabric, (c) ZnO/CuO coated PP nonwoven fabric.

ides. The mechanism of their antibacterial activity has been proposed by research workers, who attributed it to the reactive oxygen species generated by the ZnO and CuO particles [34-36], which damages the cell wall of the bacteria. Researchers have studied and found that the antibacterial activity of ZnO treated cotton fabrics was much higher [3, 4]. These results correspond to experimental observations of the quantitative bacterial reductions of our study where ZnO, CuO and ZnO/CuO coatings were applied in the nano range by the PLD technique. Another mechanism proposed involves the generation of H₂O₂, which destroys the bacteria and eliminates their proliferation, verified as a supporting mechanism for the antibacterial properties of ZnO [10].

SEM analysis of coated fabrics

From the scanning electron microscope images of the fabrics shown in **Figure 2**, one can see clearly the metal oxides coated on the fibre surface. Moreover for the coatings the extent of adhesion to the PP fibres even after plasma surface etching is comparatively lower than that of the coating on cotton gauze fabric. This may be due to the higher fibre surface area available on the yarn and surface topography of the cotton fibres. For PP nonwoven fabrics this could also mean that with a prolonged deposition time, the coverage of the coatings will increase, which, in turn, can contribute significantly to the improvement in antibacterial properties.

Surface elemental composition – EDX and XRD analysis

Figures 3.a-3.c show the EDX results for the metal oxide coatings on the hydroentangled nonwoven fabrics. It can be seen from the results that the presence of copper and zinc was detected in the coated samples examined. Adjacent tabulated data to the EDX spectrum gives the EDX results quantitatively analysed for the presence of copper and zinc.

It can be seen from the EDX results that for the ZnO coated and CuO coated PP nonwovens the presence of the respective metals is shown as a single peak, whereas for the multi-layer coated fabrics both the metal elements are represented.

The XRD analysis given in **Figure 4** shows the presence of (1 0 1), (1 0 0), (0 0 2) ZnO in the impregnated fabrics. The peaks assigned to diffractions from various planes correspond to the hexagonal close-packed structure of zinc oxide. The broadening of peaks was observed mainly due to the nano-size effect, indicating the crystallinity of the coating. The inset of **Figure 4.b** is the CuO coated fabric, which reveals CuO present in a crystalline form on the fibres. The peaks at $2\theta = 35.5$ and 38.4 are assigned to the (-111) and (111) reflection lines of monoclinic CuO nanoparticles. Since the ZnO peaks overlap the CuO peaks, it was not noticed in the case of ZnO/CuO coated fabrics.

Extended investigations with a view to envisaging the interaction of bacteria and the ZnO & CuO PLD coatings were done with the FESEM. The morphological changes that take place in the bacterial organisms when they come into contact with the ZnO and CuO coated nonwoven fabrics after a time period of 24 hrs. are presented in **Figures 5.a-5.h**. It can be seen that there has been a considerable

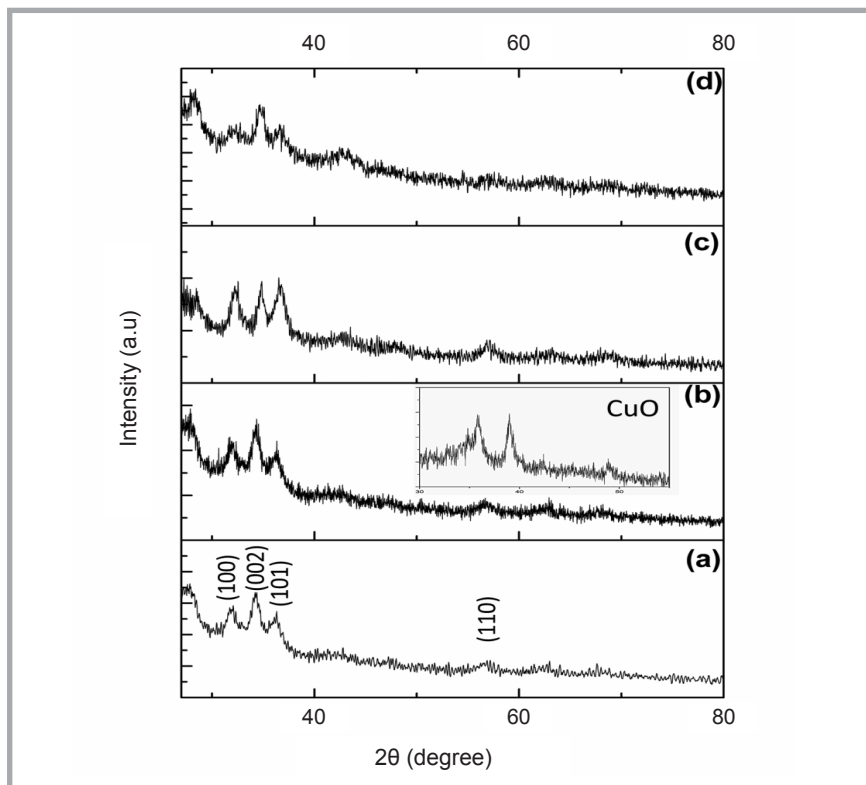


Figure 4. XRD pattern (a) ZnO/CuO coated hydroentangled PP fabric(F1), (b) ZnO/CuO coated needle punched PP fabric(Fo), (c) ZnO/CuO coated hydroentangled PP fabric(F2), (d) ZnO/CuO coated woven fabric(Fc). The inset is CuO coated fabric.

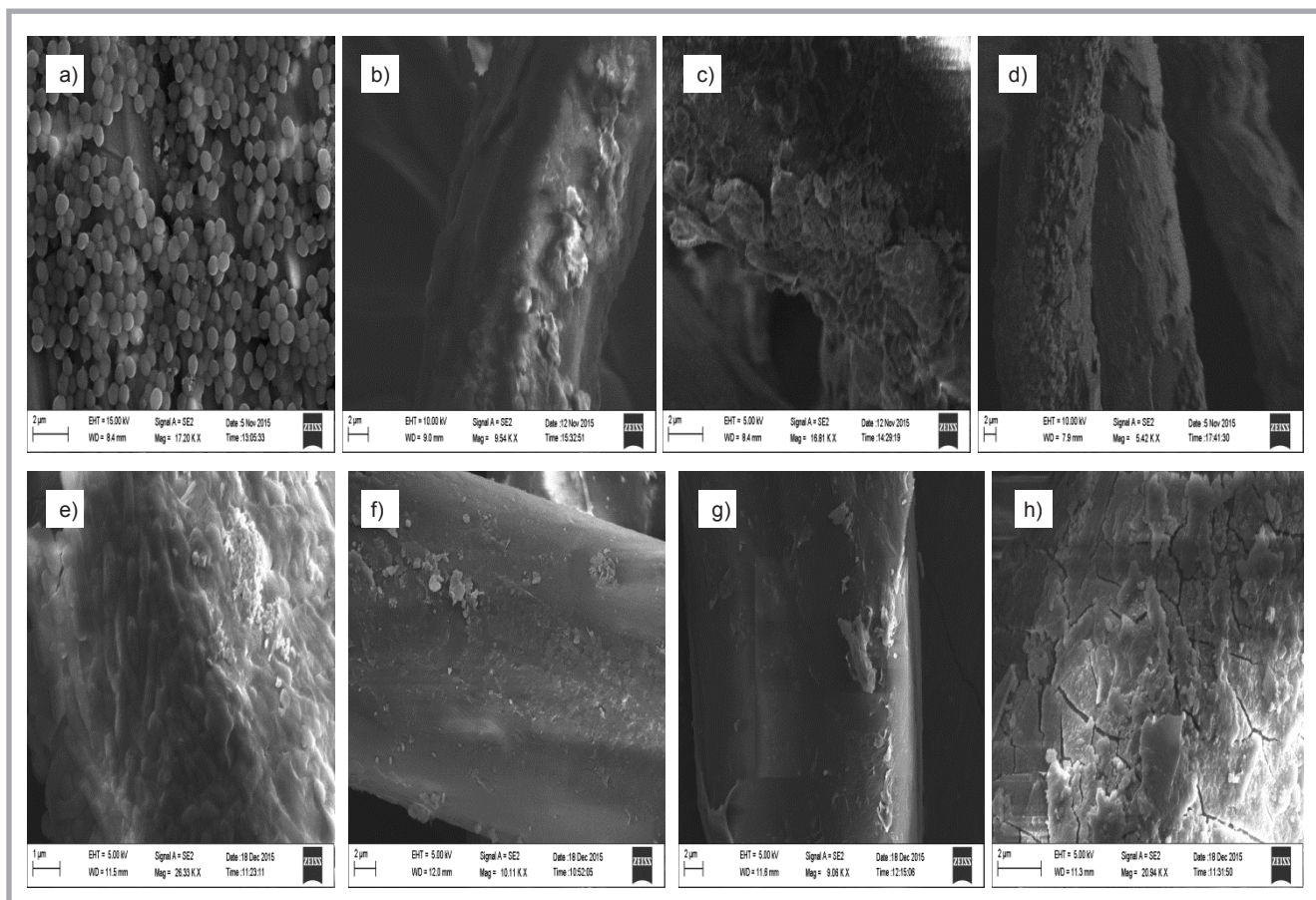


Figure 5. SEM images (a) *S.aureus* on PP nonwoven fabric, (b) *S.aureus* on ZnO coated PP nonwoven fabric, (c) *S.aureus* on CuO coated PP nonwoven fabric, (d) *S.aureus* on ZnO+CuO coated PP nonwoven fabric, (e) *E.coli* on PP nonwoven fabric, (f) *E.coli* on ZnO coated PP nonwoven fabric, (g) *E.coli* on CuO coated PP nonwoven fabric, (h) *E.coli* on ZnO/CuO coated PP nonwoven fabric.

Table 5. Capillary flow characteristics of PP nonwoven fabrics. **Note:** F1-hydroentangled PP nonwoven fabric 100 gsm, F2-hydroentangled PP nonwoven fabric 150 gsm.

Details of sample	Mean flow pore diameter, microns	Smallest flow pore diameter detected, microns	Largest flow pore diameter detected, microns
F1 Hydroentangled PP (Raw)	36.14 ± 17.56	5.62	82.48
F2 Hydroentangled PP (Raw)	42.11 ± 35.02	10.59	153.75
F1 Hydroentangled PP (Plasma treated)	35.33 ± 32.91	2.96	226.20
F2 Hydroentangled PP (Plasma treated)	42.82 ± 35.36	3.41	136.52
F1 Hydroentangled PP (ZnO coated)	112.21 ± 107.20	36.14	265.11
F2 Hydroentangled PP (ZnO coated)	75.31 ± 120.37	25.73	726.71
F1 Hydroentangled PP (CuO coated)	59.17 ± 53.85	22.38	89.33
F2 Hydroentangled PP (CuO coated)	90.43 ± 100.42	28.66	612.22
F1 Hydroentangled PP (ZnO/CuO coated)	63.09 ± 58.14	29.59	197.38
F2 Hydroentangled PP (ZnO/CuO coated)	85.15 ± 102.54	24.29	583.44

reduction in bacterial growth on the coated fibres and distinct lumping with cell wall damage has taken place with time.

Investigation of the SEM images reveals that the ZnO and CuO coatings deter bacterial growth and proliferation considerably and degrades over time, which is seen as damage to the bacterial cell structure, resulting in the antimicrobial activity of the coated fabrics.

Capillary flow analysis

The measurements of the capillary flow parameters are given in **Table 5**. From the results of uncoated and coated PP nonwoven samples it can be seen that there is a great difference in the mean flow pore diameter. There is also a significant increase in the bubble point or the largest flow pore diameter detected, which could be attributed to the opening up of pores after the coating of ZnO and CuO on the fibre surfaces, creating bigger channels of capillaries in the nonwoven fabric structure.

Summary

In this work, the possibilities of coating metal oxides on PP hydroentangled nonwovens using the pulsed laser deposition method were investigated as a means of imparting antimicrobial characteristics to them. The presence of nano-scale coatings of ZnO and CuO were established by XRD analysis. The results of antimicrobial performance assessment also demonstrated that higher antibacterial activity was exhibited against *S.aureus* than for *E.coli* for the coatings done on all the three types of fabrics studied. ZnO and CuO coated PP nonwoven fabrics can offer scope for use as wound dressings with the impregnation of suitable antibiotic drugs. Experimentation to show the direct interaction of the

bacterium and surface metal oxide coatings of ZnO and CuO by FESEM analysis showed death as well as lower presence and decomposition over time. PP, being inherently non-toxic, has excellent biological and chemical resistance, and the use of specialised PP fibres for hydroentangled nonwoven fabrics contributes to a soft, high-strength, light weight, larger surface area material with good wicking properties for use in the medical textile industry. Measurements of pore characteristics of the coated fabrics tend to show that the thin metal oxide coatings adhere to the fibre surfaces and the mean pore diameter increased significantly compared to the uncoated samples. In addition to metal oxide coatings, as proposed by Petruelyte [37], nano-scale biological materials such as enzymes and drugs could add specific functionality to medical textiles.

Acknowledgement

The authors gratefully acknowledge the help of M/s FiberVisons a/s, Denmark for providing the PP Hy-Entangle fibre material that has been used in this study. They also thank the Directors of SITRA, Coimbatore and CECRI, Karaikudi for their support and guidance.

References

1. Badrossamay MR and Sun G. Rechargeable biocidal polypropylene prepared by melt radical grafting of polypropylene with Diaboxyl amine triazine. *European Polymer Journal* 2008; 44, p.733.
2. Vohrer V, Muller M and Oehr C. *Surface and coatings technology*, 1998, 98,12.
3. Gulrajani L and Deepti G. Emerging trends for functional finishing of textile. *IJFTR* Dec 2011; 388-397.
4. Jeong SH, Yeo SY and Yi SC. The effect of filler particle size on the antibacterial

- properties of compounded polymer/silver fabrics. *Journal of Materials Science* 2005a; 40(20): 5407.
5. Jeong SH, Hwang YH and Yi SC. Antibacterial properties of padded PP/PE nonwoven incorporating nano-sized colloids. *Journal of Materials Science* 2005b; 40(20): 5413.
6. Borkow G and Gabbay J. Copper as a biocidal tool. *Current medicinal chemistry* 2005; 12(18): 2163.
7. Radesh kumar C and Munstedt H. Antimicrobial polymers from PP/Silver composites-Ag release measured by anode stripping voltametry. *Reactive and functional polymers* 2006; 66(7): 780
8. Kumar R and Munstedt H. Silver ion release from antimicrobial polyamide/silver composites. *Biomaterials* 2004; 26(14): 2081.
9. Wang Hong-Bo, Wang Jin-Yan, Wei QU-Fu, Hong Jian-Han and Zhao Xiao-Yan. Nanostructured antibacterial silver deposited on polypropylene nonwovens. *Surface review and letters*, 2007; 14, 4: 553-557. @world scientific publishing company.
10. Padmavathy N and Vijayaraghavan R. Enhanced bioactivity of ZnO nanoparticles-an antimicrobial study. *Science and technology of advanced materials* 2008; 9, 035004 (7pp).
11. Yadav A, Virendra Prasad, Kathe AA, Sheela Raj, Deepti Yadav, Sundaramoorthy and Vigneshwaran N. Functional finishing in cotton fabrics using zinc oxide particles. *Bull of Mat Sci* 2006;29,6: 641-645.
12. Kathirvelu S, D' Souza L and Dhurai B. A study on functional finishing of cotton fabrics using nano particles of zinc oxide. *Mat Science* 2009;15: 75.
13. Hyde GK and Hinestroza JP. *Nanofibers and nano technology in textiles*, Woodhead publishing, Cambridge, UK, 2007; p.428.
14. Luzinov I. *Nanofibers and nano technology in textiles*. Woodhead publishing, Cambridge, UK, 2007,p.448.
15. Egami Y, Suzuki K, Tanaka T, Yasuhara T, Higuchi E, Inou H. *Synthetic metals*, 2011; 26, p.135.
16. Najar SS, Kaynak A, Foitzik RC. *Synthetic metals*, 2007; 157, p.1.
17. Vihodeeva S, Kukle S, Barloti J. *IOP Series: Material science and engineering* (IOP Publishing), 2011, 23, 012037.
18. Jur JS, Sweet WJ (III), Oldham CJ, Parsons GN. *Adv Funct Mats* 2011; 21: 1948.
19. Shishoo R. *Plasma technologies for textiles*, Woodhead publishing, Cambridge, UK,2007,p.165
20. Reddy KM, Feris K, Bell J, Wingett DG, Hanley C and, Punnoose A. Selective toxicity of Zinc oxide nanoparticles to prokaryotic and eukaryotic systems. *App Physics* 2007; 90: 213902-213903.
21. Abramov OV, Gedanken A, Koltypin Y, Perkas N, Perelshtein I, Joyce E, Mason TJ. Pilot scale coating of nanoparticles onto textiles to produce biocidal fabrics. *Surface and coatings Technology* 2009; 204: 718-722

22. Yamada H, Suzuki k and Koizumi S. *Gene expression profile in human cells exposed to zinc* 2007; 32: 193-196
23. Sharma D, Rajput J, Kaith BS, Kaur M and Sharma S. Synthesis of ZnO nanoparticles and study of their antibacterial and antifungal properties. *Thin solid films* 2010; 519, 1224-1229.
24. Sawai J. Quantitative evaluation of antibacterial activities of metal oxide powders (ZnO, MgO and CaO) by conductimetric assay. *Jour of Microbiol Meth* 2003; 54: 177-182.
25. Rajendran R, Balakumar C, Hasabo AM, Jayakumar S, Vaideki K and Rajesh E M. Use of zinc oxide nano particles for production of antimicrobial textiles. *Int Jour of Engg, Sci and Tech* 2010; 2, 1: 202-208.
26. Stoimenov PK, Klinger RL, Marchin GL. Metal oxide nanoparticles as bactericidal agents. *Langmuir* 2002; 18: 6679-6686.
27. Zhang W, Ji JH, Zhang H, Zhao J, Yan W and Chu PK. Antimicrobial properties of copper plasma-modified polyethylene, *Polymer* 2006c; 47(21): 7441.
28. Yeo YS, Lee HJ and Jeong SH. Preparation of nanocomposite fibres for permanent antibacterial effect, *Jour Mater Sci* 2003; 38: 2413.
29. Yamamoto O, Hotta M, Sawai J, Sasamoto T and Kojima H. Influence of powder characteristic of ZnO on antibacterial activity-effect of specific surface area. *Jour Ceram Soc Jpn* 1998; 106: 1007.
30. ASTM F-316-03, Standard Test Methods for Pore Size Characteristics of Membrane Filters by Bubble Point and Mean Flow Pore Test .
31. OIE Terrestrial Manual 2012, Guideline 2.1, Laboratory methodologies for bacterial antimicrobial susceptibility-testing, <http://www.oie.int/enour-scientific-expertise/reference-laboratories/list-of-laboratories/>
32. ASTM E2149-01:2010, Standard test method for determining the antimicrobial activity of immobilized antimicrobial agents under dynamic contact conditions.
33. Singh G, Joyce EM, Beddow J and Mason TJ. Regular Article-Evaluation of Antibacterial Activity of ZnO Nanoparticles Coated Sonochemically onto Textile Fabrics. *Biotechnology and Food Sciences* 2012; 2(1): 106-120.
34. Zhang LL, Jiang YH, Ding YL, Povey M and York D. Investigation into the antibacterial behaviour of suspensions of ZnO nanoparticles (ZnO nanofluids). *Jour Nanopart Res* 2007; 93: 479.
35. Shantikumar N and Abilash S. Role of size scale of ZnO nanoparticles and micro particles on toxicity towards bacteria and osteoblast cancer cells. *Mater Sci* 2008;5: 3548.
36. Textor T, Farouk A, Moussa A, Ulbricht M and Schollmeyer E. ZnO modified hybrid polymers as an antibacterial finish for textiles. *TRJ* 2014; 84(1): 40.
37. Petruyte S. Advanced textile materials and biopolymers in wound management. *Danish Med Bull* 2008; 55(1): 72.

□ Received 19.08.2015 Reviewed 01.02.2016



LODZ UNIVERSITY OF TECHNOLOGY
DEPARTMENT OF KNITTING TECHNOLOGY
AND

POLISH TEXTILE ASSOCIATION

SCIENCE & TECHNOLOGY CONFERENCE

Knitt Tech 2017

in the fields of:

INNOVATIVE TECHNIQUES AND TECHNOLOGIES IN KNITTING

21-23 September 2017

Place of the conference: RESORT ŁAZIENKI II, CIECHOCINEK, POLAND

CONFERENCE SCOPE AND OBJECTIVES

The Knitting Conference Knitt Tech 2017 is a continuation of previously conducted business meetings of the representatives of knitting industry and companies specialized in making-up of knitted garments with manufacturers of textile machinery and equipment, representatives of finishing companies, scientists, members of the broadly understood sector of public administration responsible for EU programs, representatives of banks and leasing funds.

The aim of the conference is to promote and exchange knowledge in the area of innovative technologies of knitted garments and technical products, new trends in the sector of raw materials, hosiery and underwear, as well as computer CAD systems for knitwear designing.

The conference agenda also includes the issues of finishing and refining processes, giving the knitted fabrics new functional and utility features. The problems concerning market analysis, production profitability and efficiency in obtaining financial support from sectoral, regional and national programs will also be discussed.

The papers concerning current fashion trends in knitted fabrics and garments, as well as effectiveness of marketing activities in small and medium-size companies will definitely add attractiveness to the conference.

In addition, the conference is intended to be a discussion forum, where participants can share experiences and exchange views on the external factors influencing the knitting industry in Poland.

This time the meeting will be held in one of the most beautiful palaces in Ciechocinek, and the organizers will traditionally make every effort to run it in a relaxed atmosphere.

Conference Secretary:

D.Sc. Katarzyna Piekłak

phone: +48 42 631-33-38

e-mail: konferencja.dziewiarska@info.p.lodz.pl