World Applied Sciences Journal 32 (3): 392-398, 2014
ISSN 1818-4952

DOI: 10.5829/idosi.wasj.2014.32.03.14528

Imparting Permanent Antibacterial Properties to Viscose Fabric Using Zinc Oxide Nanoparticles and Polymeric Binders

M. Salama and A.A. El-Sayed

Textile Research Division, National Research Centre, Dokki, Giza, Egypt

Abstract: The present work describes the effects of applying some polymeric binders on viscose fabric to enhance chelation of nano ZnO for imparting antibacterial activity against *E. coli* and *Staphylococcus aureus*. Viscose fabrics were primarily padded with the polymeric binders. Optimization of the binder concentration was reported. Viscose fabric pretreated with certain polymeric binders namely, Polyvinylpyrrolidone (PVPO), poly-4-vinyl pyridine (PVP) or reactive polyurethane resin (PU) and after treated with nano zinc oxide show superior reduction in the bacterial growth even after 30 washing cycle, in comparison with those fabrics treated only with nano zinc oxides. The particle size of the prepared nano zinc oxide was assisted with XRD. The interaction between the nano zinc oxide, polymer binders and fabrics was evaluated by nitrogen content analysis and atomic absorption spectroscopy.

Key words: Antibacterial activity · nanotechnology · Polymeric binder · Viscose · Zinc oxide

INTRODUCTION

Increasing awareness of general sanitation, contact disease transmission and personal protection, has led to the development of fabrics with antimicrobial property. The fabrics are engineered to protect users against the spread of bacteria and disease rather than to protect the quality and durability of the textiles. Most of the processes to create antibacterial fabrics invariably require the attachment of biocidal or bacteriostatic agents to the fabric surface [1-6]. The technology that deals with the science and engineering of materials at dimensions of roughly 1 to 100nm in length is referred to as nanotechnology [7-9]. The resulting unique properties of nanoparticles cannot be anticipated from a simple extrapolation of the properties of bulk materials [10, 11]. The inherent properties of the textile fibers provide room for the growth of micro-organisms. In addition, the staining and loss of the performance properties of textile substrates are the results of microbial attack. With a view to protect the wearer and the textile substrate itself, antimicrobial finishing is applied to textile fabrics [12]. Zinc oxide has been considered as a promising nanomaterial for a variety of useful applications [13, 14]. ZnO is currently regarded as an antibacterial agent against both Gram negative microorganism like *E. coli* and Gram positive microorganism like *Staphylococcus aureus* in microscale and nanoscale formulations [15-19].

The aim of the present work is to impart permanent antimicrobial properties to viscose fabric using ZnO nano sol and different types of polymeric binders. The preparation of ZnO and treatment condition of it to viscose fabric has been explored. Antimicrobial properties efficiency of the treated viscose fabric regarding gram positive and gram negative and its durability even after 30 washing cycles have been evaluated.

MATERIALS AND METHODS

Materials: Pure viscose fabric plain weaved, scoured and unfinished, was supplied by Abou El-Ola for Spinning and Weaving, 10th of Ramadan, Egypt. Fabric weight is 110 gm/m^2, number of warps is 375 threads/10 cm and number of weft is 320 threads/10 cm. Zinc acetate $(CH_3COO)_2Zn.\ 2H_2O$, sodium hydroxide pellets (99% NaOH) and methanol are from International Industrial Company, Cairo, Egypt. Polyvinylpyrrolidone, (C_6H_9NO) X, from Sisco Research Laboratories PVT, India.

Corresponding Author: M. Salama, Textile Research Division, National Research Centre, Dokki, Giza, Egypt.

Poly-4-vinyl pyridine from Aldrich, USA and Protolane 367 (reactive polyurethane resin) are used, all chemicals are of laboratory grade.

Preparation of Nano Zinc Oxide: The typical procedure for the synthesis of ZnO sol is based on the method described in the literature [20, 21]. In a typical procedure, 0.01 mole of zinc acetate dihydrate was dissolved in 50 ml of methanol and heated at 50°C along with stirring for half an hour, thus making precursor solution (A). 0.02 mole of sodium hydroxide was dissolved in 50 ml of methanol and heated at 50°C along with stirring for 1 h, making precursor solution (B). In order to make ZnO nano sol, solution (B) was added into the solution (A) dropwise under constant stirring for half an hour and then the mixture was heated at 50°C for further half an hour. Subsequently, after continuous stirring for 2 h and cooling at room temperature, a homogenous and transparent sol was obtained.

Scouring of Viscose Fabrics: Viscose fabrics were scoured before treatment using 2g/l sodium carbonate and 1g/l non-ionic detergent at 80°C for 15 min followed by thorough rinsing with cold water and finally air dried at ambient temperature.

Coating of Viscose Fabric with Polymers: The viscose fabric was treated with aqueous solutions containing different amounts of polyurethane (PU), poly-4-vinyl pyridine (PVP), or Polyvinylpyrrolidone (PVPO) by dip-pad-dry-cure technique. The fabric is dipped for 1 min in the polymer solution and then padded using an automatic press at a nip pressure of 2.75 kg/cm^2 to obtain 80% wet pickup, dried in ambient air and then cured at 140°C temperatures for 3 min.

Loading of ZnO Nano Sol onto Viscose Fabric: The viscose fabric was mounting through dip- pad-dry-cure technique by the Zn $(OH)_2$ nano sol for 5 min and then padded using an automatic press at a nip pressure of 2.75 kg/cm^2 to obtain 80% wet pickup. The prepared samples were then placed at 70°C in pre-heated oven to remove the solvent from the fibers and then heated at 150°C for 5 min, to complete the formation of zinc oxide from the precursor. Finally, the impregnated fabric was rinsed with deionized water and non-ionic detergent (2g/l at 40°C for 10 minutes). During this step the unattached ZnO particles were removed out from the fiber surface.

X-ray Diffraction (XRD): The XRD pattern of nano zinc oxide powder was recorded by using PAN Analytical X Pert PRO X-ray diffractometer and CuKa radiation (λ=1.5406 Å) as X-ray source. The measurements were carried out at a scanning rate of 8°/min in 2θ range of 20°-80° (θ being the angle of Bragg's diffraction). The peak width at half maximum (FWHM) in the XRD has been used to determine the crystal diameter according to Deby-Scherrer formula:

$$D = \frac{K\lambda}{\beta \cos\theta}$$

Where: K = (0.9) is the Scherrer constant; λ (=0.15406 nm), the x-ray wave length; β is the peak width of half maximum; and θ is the Braggs diffraction angle and D is the grain size.

Bacterial Resistance Test: The antibacterial properties of untreated viscose fabric and viscose fabric treated with polymeric binders and/or with nano zinc oxide were quantitatively evaluated by using plate count agar technique according to the American Association of Textile Chemists and Colorists (AATCC) test method 100-1999. The species of microorganisms used in this experiment were *E. coli* AATCC 2666 (Gram-ve) and *Staphylococcus aureus* AATCC 6538 (Gram +ve). The bacteria were individually inoculated into tubes containing 5 ml BHI (Brain heart infusion) broth sterile suspension. Such suspension was adjusted to 0.5 McFarland standards. A small volume of the previous microorganism's inoculums (10µl) was transferred to sealed jar containing 1gm of fabric sample in addition to 50 ml normal saline. The jars were incubated at 37°C for 24 hours. (10µl) of previous suspension were transferred on nutrient and Sabouraud dextrose agar for microorganism colonies count.

The reduction of bacteria R (%) was calculated using the following equation:

$$R(\%) = \frac{A - B}{A} \times 100$$

Where: A is the number of bacteria colonies from untreated control specimen after inoculation at zero contact time, B the number of bacterial colonies from treated specimen after inoculation over 24 h.

Elution of Metalized Viscose Samples: 2-3 gram sample of the nano zinc oxide mounted fabrics were treated with 80-90 ml of 0.5N HCl and heated to 95°C for 20 min. The amounts of the eluted zinc ions were measured using atomic absorption spectrometer (VARIAN AA220).

Wash Fastness: The washing durability test method for the treated fabrics was assessed according to the AATCC test method 61-2003. Washing was performed using a home laundering machine at 50°C in a stainless steel lever lock container. The fabrics were leached in 0.15% aqueous solution of sodium lauryl sulphate detergent and in the presence of 50 steel balls for 45 min. The substrates were then rinsed intensively with water and dried at room temperature prior to further investigations.

Nitrogen Content Determination: The nitrogen content of polyurethane (PU), poly-4-vinyl pyridine (PVP) and polyvinylpyrrolidone (PVPO) was determined using the elemental analyzer, Germany Elemental Analyses system, GmbH, Vario EL III.

RESULTS AND DISCUSSION

X-ray Diffraction (XRD): Figure 1 represents the X-Ray diffraction pattern of nano ZnO. The peaks assigned to diffractions from various planes correspond to hexagonal close packed structure of zinc oxide. This confirms the presence of ZnO in the synthesized material. The broadening of peaks was observed and it is mainly due to nano-size effects [22, 23]. The XRD pattern of this sample indicates that the synthesized ZnO particles on the fiber surface are found hexagonal wurtzite crystal phase due to the presence of the attributive peaks at 2θ=31.71°, 34.48°, 36.23°, 47.53°, 56.47°, 62.78° and 67.92°. The peaks assigned to diffractions from various planes are corresponding to hexagonal close packed structure of zinc oxide [20]. The average grain size of the prepared zinc nano particles was 42±11 nm as calculated.

Effect of Binder Type and Concentration on Antibacterial Property: Viscose fabrics treated with different polymeric binders (polyurethane, polyvinylpyrrolidone and

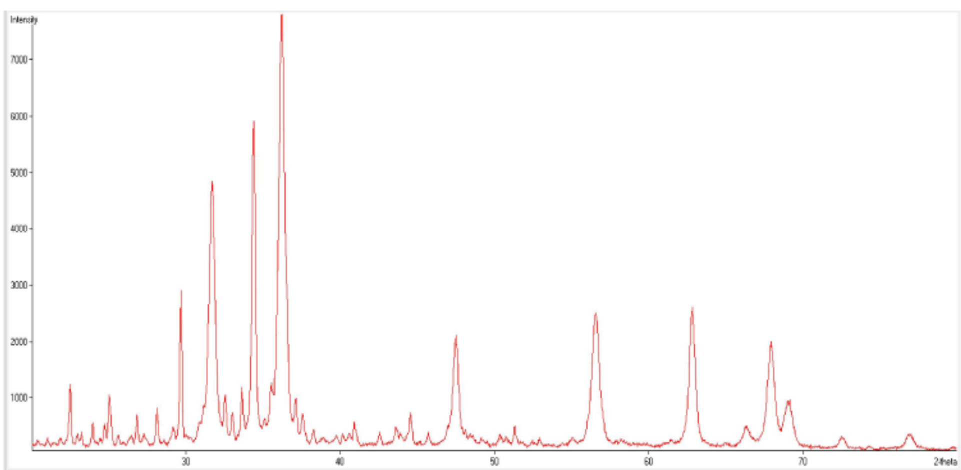

Fig 1: XRD pattern of nano zinc oxide

Table 1: Effect of binder type and concentration on the *Staphylococcus aureus* growth.

		Bacterial reduction (%)		
Polymer concentration (%)	ZnO nano sol (%)	PU	PVPO	PVP
Zero	Zero	0.0	0.0	0.0
Zero	0.99	92.0	92.0	92.0
0.5	Zero	0.0	0.0	0.0
0.5		99.9	99.9	99.9
1.0		99.9	99.9	99.9
1.5	0.99	97.1	96.4	94.0
2.0		93.0	93.1	91.1

Table 2: Effect of binder type and concentration on the *Escherichia coli* growth.

		Bacterial reduction (%)		
Polymer concentration (%)	ZnO nano sol (%)	PU	PVPO	PVP
Zero	Zero	0.0	0.0	0.0
Zero	0.99	77.0	77.0	77.0
0.5	Zero	0.0	0.0	0.0
0.5		91.9	88.9	84.9
1		99.9	99.9	94.9
1.5	0.99	93.5	90.2	88.1
2		85.5	84.2	80.1

Table 3: Nitrogen content of PU, PVP and PVPO.

Polymer	Nitrogen content %
Polyurethane [PU]	20.65
Polyvinylpyridine [PVP]	4.63
Polyvinylpyrrolidone [PVPO]	10.69

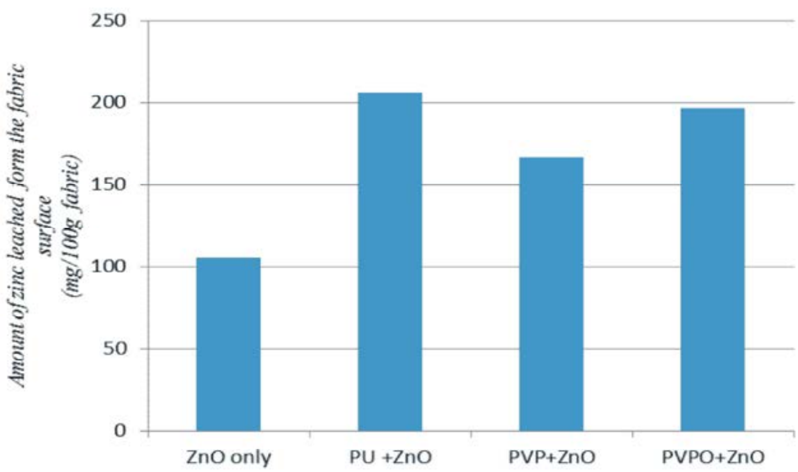

Fig 2: Effect of polymer type on the amount of zinc oxide absorbed by the viscose fabric (polymer concentration 1%)

polyvinylpyridine) at different concentrations and after treated with ZnO nano sol were challenged to kill bacteria. The results presented in Tables 1 and 2 indicate that both the untreated and binder treated viscose fabric do not exhibit antibacterial activity. On the other hand, treatment of viscose fabrics with nano zinc oxide results in superior reduction in the bacterial growth regardless of the bacteria type. The dominant mechanisms of such bacterial resistance are found to be either or both of chemical interactions between hydrogen peroxide and the bacteria membrane proteins and/or the chemical interactions between other unknown chemical species generated due to the presence of ZnO nanoparticles with the lipid bilayer [2]. Data in Tables 1 and 2 also revealed that complete bacterial reduction could be attained using PU, PVP or PVPO polymers at 1% concentration. The higher ability of polyurethane and polyvinylpyrilidone in bacterial reduction could be attributed to their higher nitrogen content in comparison with poly polyvinyl pyridine, thereby enhancing of ZnO nano sol fixation on the treated viscose (Table 3).

This assumption is probably confirmed from the atomic absorption measurements of the eluted ZnO form the fabric surface (Fig. 2). It is also worth noting that, the relatively high amount of ZnO absorbed by Polyvinylpyrrolidone could be attributed to the contribution of the oxygen atom of the pyrilidone ring in attraction of nano ZnO [24]. It is also noted from the set results, that the higher concentrations of the polymers used lead to decrease in the percentage of bacterial reduction. This could be due to the aggregation of the nano zinc oxide on the polymer surface and losing the advantage of the nano size.

Table 4: Washing fastness against growth of *Staphylococcus aureus*.

Treatment	Reduction in the growth of *Staphylococcus aureus* (%) after different washing cycles			
	5 cycles	10 cycles	20 cycles	30 cycles
ZnO only	92.0	89.5	67.4	41.0
PU & ZnO	99.9	99.0	97.4	94.9
PVPO& ZnO	99.9	98.6	96.1	94.2
PVP& ZnO	99.9	98.0	94.7	92.8

Table 5: Washing fastness against growth of *Escherichia coli*.

Treatment	Reduction in the growth of *Escherichia coli* (%) after different washing cycles			
	5 cycles	5 cycles	5 cycles	5 cycles
ZnO only	73.1	66.3	43.7	32.2
PU & ZnO	99.4	95.7	88.9	84.1
PVPO& ZnO	99.3	94.1	86.3	82.1
PVP& ZnO	94.0	93.6	88.3	81.8

Table 6: Leaching of nano ZnO on viscose fabrics after washing cycles.

Treatment	ZnO leached (mg/100g fabric)		
	Before washing	30 washing cycles	ZnO loss (%) after 30 washing cycles
ZnO	125.5	34.9	72.1
PU + ZnO	205.8	180.0	12.5
PVPO + ZnO	196.8	178.0	9.5
PVP + ZnO	167.0	153.0	8.3

Washing Fastness: Viscose fabrics treated with 1% PU, PVPO or PVP solution followed by treatment with nano ZnO were subjected to different washing cycles to investigate their capability to resist the bacterial growth after washing. Data presented in Tables 4 and 5 show that, viscose fabrics treated with polymer binders and after treated with nano zinc oxide then subjected to 30 washing cycles exhibit superior reduction in the bacterial growth, in comparison with those fabrics treated only with nano metal oxides. Such trend could be attributed to high fixation of the nano zinc oxide on the fabrics treated with the polymer binders. The nitrogen atoms in the polymer chain are not only acting as attracting groups for the nano zinc oxides, but also fixing them on the fabric. This fact could be the reason behind the ability of the viscose fabrics, treated with either of the three polymer binders and nano zinc oxides, to maintain high antimicrobial activity even after 30 washing cycles.

Leaching Nano ZnO on Viscose Fabrics after Washing Cycles: Viscose fabrics coated with the three aforementioned polymers and treated with nano zinc sol were subjected up to 30 washing cycles. The amount of the absorbed zinc oxide was leached from the fabric and measured. Once more, data in Table 6 are in supportive manner with data of table 5, the used polymers (polyurethane, Polyvinylpyrrolidone or polyvinylpyridine) are not acting only as an attracting layer for the nano zinc, but also as fixative agents. Such feature could be the reason behind the unique ability of the treated fabrics to sustain the bacterial resistance in comparison with the viscose fabrics treated only with nano ZnO. It is also worth noting that, despite the lower ability of PVP to attract ZnO in comparison with the other two polymers, it shows minimal loss in nano zinc oxide after washing. This observation indicates the ability of the pyridinium ring to form stable and strong interaction with nano ZnO.

CONCLUSION

An x-ray diffraction (XRD) study of the prepared nano zinc oxide confirms the presence of ZnO in the synthesized material, with a particle size of 42±11 nm. Treatment of viscose fabrics with nano zinc oxide results in superior reduction in the bacterial growth towards *E. coli* and *Staphylococcus aureus*. Complete bacterial reduction could be attained using PU, PVP or PVPO polymers at 1% concentration and the higher ability of polyurethane and polyvinylpyrilidone in bacterial reduction could be attributed to their higher nitrogen content in comparison with poly polyvinyl pyridine.

Higher concentrations of the polymers used lead to a decrease in the percentage of bacterial reduction and could be referred to the aggregation of the nano ZnO on the polymers surface, losing the advantage of the nano size. Viscose fabrics treated with polymer binders and after treated with nano metal oxides and subjected to 30 washing cycles, show superior reduction in the bacterial growth, in comparison with those fabrics treated only with nano ZnO. This fact could be attributed to the nitrogen content in the polymer chain, which are not only acting as attracting groups for the nano zinc oxides, but also fixing them on the fabric. Despite the lower ability of PVP to attract zinc oxide, in comparison with the other two polymers, it shows minimal loss of nano zinc oxide after washing, indicating the ability of the pyridinium ring to form stable and strong interaction with nano zinc oxide.

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