Multi-Functional Finishing of Woolen Fabric

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Abstract

The improvement of the fabric properties considers the most important reasons for textile functionalization. The present study focuses on one finishing bath for imparting durable multifunctional properties such as wet crease recovery angle, antibacterial and ultraviolet (UV) protection to wool fabrics. Polyurethane (PU) and zinc oxide (ZnO) mixture finishing bath were selected to treat wool fabric at the different concentrations of the finishing agents as well as the curing temperatures and curing times were studied. The results revealed that the finished wool fabric have a high bacterial reduction percent against two tested bacteria Gram negative bacteria (*Escherichia coli*) and Gram positive bacteria (*Staphylococcus aureus*) in addition to enhance the wet crease recovery even after twenty washing cycles. The surface of treated wool fabrics was characterized by Scanning Electron Microscope (SEM) and Electron Dispersion Emission X-ray (EDX). Also the effect of the treatment on physico-mechanical properties was evaluated. The treated wool fabrics gave an excellent protection against the UV radiation. The stiffness, the resistance to tear, air permeability and wettability increased after the treatment of wool fabrics with PU/ZnO and there isn't a significant change in the tensile strength. Effect of PU, ZnO and their mixture on the dyeing properties of wool fabric was studied as well as the colorfastness of dyed fabrics.

Keywords: Wool, Polyurethane, Zinc oxide, Wet crease recovery angle (WCRA), Antibacterial, Ultraviolet protection (UPF).

Introduction

In recent years, many researchers around the world are interested in the field of functional textiles as it had become an important feature in the textile industry. The dynamic development of functionalized textile products is directly related to progress in chemistry and polymer processing **[T. Jesionowski,2011]**.

Novel finishes of high added value to apparel fabrics are also greatly appreciated by a consumer market **[R. Perumalraj,2013]**. All the leading textile industries are focusing on value added applications of new properties or combinations of properties, e.g. antibacterial, absorbing UV radiation or crease recovery, wettability fabrics, etc... Wool is a biodegradable animal fiber, which is usually considered as a high quality expensive textile material. It is especially known for its comfort, warmth effect, moisture retention and good dry crease recovery angle. Wool exhibits poor antimicrobial activity, wet crease recovery and weak dimensional stability under multiple launderings as well wool fabrics will be good media for

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generation and propagation of microorganisms **[M. Mohsin,2014]**. The microorganisms can be resulted in damages, skin irritations, and infections in wool products **[H. Y. Ki,2007]**,**[J. Chang,2012]**, **[S. M. Abo El-Ola,2007]**. For these reasons, the wool materials must be protected against microorganisms in order to suppress their growth and dissemination as well as fiber damage **[H. Y. Ki,2007]**.

Low wet easy-care performance of the wool fabric was due to the comparatively less inter fiber bonding and more swelling in the wet state **[M. Mohsin,2014]**. The improved wet wrinkle recovery of the wool fabric obtained with the surface post-application of a polymer is attributed to the formation of inter fiber and inter yarn connections. It was suggested that the elastic connections stretched when the fabric was deformed and then during recovery, so the fabric overcome the deformation. This restricts the movement of the fiber in bending, so there is increase in bending rigidity such elastic fiber-fiber connections contribute load-bearing elements to the fabric so that inhibit of the fiber movement and aid increase recovery from deformation as well as decrease the residual strain after deformation **[H. Yi,2008]**. Likewise, intrinsic surface hydrophobic features of wool are the most important problems which have negative influences on different aspects of wool and prompt scientists to find a solution over the past decades, so it is very important to modify this inherent problem **[M. A. Shirgholami,2015]**. Hydrophobic surfaces, caused by fatty layer of the wool fibers, are another challenge in the use of wool fibers. The water absorption and sweat venting properties of wool fiber are destroyed by the hydrophobic surface; therefore, result in poor wearing comfort of the wool textiles **[J. Chang,2012]**.

ZnO is one of non-toxic and safe antibacterial agents to the human being, and can kill many harmful microorganisms. The lack of toxicity, the lack of adverse effects on human cells and the low price are the most important advantages of ZnO. It was found that a layer of ZnO deposited on medical textile materials has strong bacterial resistance against *Escherichia coli* bacteria (*E. coli*), *Staphylococcus aureus* (*S. aureus*) and *Pseudomonas aeruginosa* (*P. aeruginosa*) - in patients undergoing hospitalisation. So scientists are trying to deposit ZnO using different methods with different textile substrates in order to inhibit and/or kill the bacteria, fungi and viruses **[H. Teterycz,2014]**.

In addition to that, ZnO belongs to a group of compounds with photo-catalytic properties **[J. Sójka-Ledakowicz,2008]**, which are able to provide good protection by reflecting and/or scattering most of the UV-rays, additionally ZnO absorb UV radiation due to its property as semi conductive materials **[H. Yang,2004]**,**[M. Hashem,2013]**,**[R. M. Kotb,2014]**. Easy application of ZnO as antimicrobial agents and anti-UV ray could be lost during laundering, So it is very important to use synthetic resin such as PU **[Y. L. Lam,2012]** as self-crosslinking binder to assists the attachment of ZnO which will be confined in the network structure of PU resin with the fabric surface **[Y. L. Lam,2012]**,**[Y. L. Lam,2013]**.

PU basic polymer is (strong, rigid) and (soft, elastic). Polyurethanes belong to the group of very durable plastic material. it has wide applications, It can be coated to textiles, leather, in solution, dispersion, with a low solvent content or without it, as granules or powder. PU has good adhesion to the fabric, good durability at low temperatures, also it can be used without softeners, it characterized by good viscosity, abrasion resistance, as well as it has pleasant and soft handle, repellent to oils and fats **[P. Durst,1985]**.

So, this work aims to impart wool fabrics multifunctional properties as antibacterial, wet crease recovery, UV protection as well as wettability by using PU/ZnO mixture.

Materials and Methods

2.1. Materials

2.1.1. Fabrics

A plain weave wool fabric of 146 g/m² with 25 ends / cm and 24 picks / cm was purchased from Goldentex Company.

2.1.2. Chemicals

BAYPRET® USV (PU) as self-crosslinking polymer was supplied from "TANATEX chemicals", ZnO, Glauber's salt (hydrated sodium sulphate), sodium carbonate, acetic acid and nonionic detergent were purchased as laboratory grade chemicals to use in this work.

2.1.3. Microorganisms used

A Gram-positive *Staphylococcus aureus (S.aureus)* and a Gram-negative *Escherichia coli (E.coli)* were used in this research.

2.1.4. Media used

Nutrient broth/ agar medium: contains beef extract (3g/L), peptone (5g/L) for solid medium (15 g/L) agar was added.

2.1.5. Dyes

The *Supranol violet RWN01* acid dye with color index *Acid Violet 48* was used in this study to dye wool fabric. It was supplied from "Dystar Co.". The wavelength (λ_{max}) of this dye is *600 nm*, molecular structure is *anthraquinones* and its chemical structure is shown in Fig. (1)
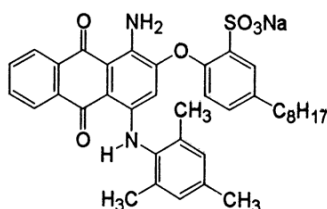

Figure (1): Chemical structure of acid dye

2.2. Methods

2.2.1. Fabric scouring

Wool fabric was scoured using sodium carbonate (2g/l) and nonionic detergent (5g/l) at 40°C for 20 min in a material to liquor ratio 1:50 , the fabric was thoroughly washed several times with cold water. Finally was squeezed and dried at ambient temperature.

2.2.2. Finishing bath formulation

Wool samples were impregnated with an aqueous solution and subjected to pad-batch-cure technique as follows: PU concentrations on the weight of the bath (25 – 100 g/l o.w.b.), ZnO concentrations (1-9 g/l o.w.b.) in single bath. Fabric samples were padded through two dips and two nips in the prepared solution to a wet pick up of ca 100% on the weight of the fabric (o.w.f.). The fabrics are then batched, in plastic film for 2 hours and covered with a plastic film. The fabric was then cured at (100-130°C) for (2-5 min). The cured fabric was washed with nonionic detergent (2g/l) at 40°C for 10 min, and then was washed with tap water finally dried at room temperature. Otherwise the finishing formulation illustrated elsewhere.

2.2.3. Dyeing

Blank and finished wool samples were dyed by acid dye (Acid Violet 48) through exhaustion method by using technical data sheet of manufacturer instructions. Material to liquor ratio (1:50), the dye shade (2%) (o.w.f), pH (4.5-5) was adjusted by using 60% acetic acid, Glauber's salt (hydrated sodium sulphate) 2g/l (o.w.b). The wool fabrics were dyed through two approaches: dyeing before finishing and dyeing after finishing.

Dyeing time and temperature were adjusted according to the following manufacture chart in Fig. (2)
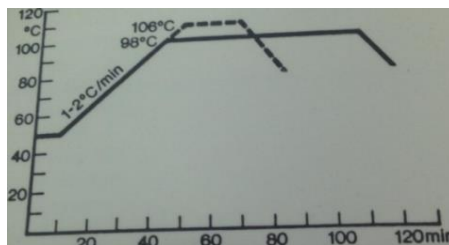

Figure (2): Manufacture chart of acid dyes

3. Testing and analysis

3.1. Durability test

The treated samples were washed for 5 and 20 washing cycles according to AATCC test method (124-2006). After these washing cycles the samples were evaluated for wet crease recovery and antibacterial activity.

3.2. Wet crease recovery angle

The crease recovery angles (CRA) of fabrics was determined according to ASTM procedure (D/1295-67-1972). For the wet crease recovery angle (WCRA) measurement, the test fabric samples were immersed in distilled water containing 2 g/l nonionic wetting agent and the excess liquid was removed between sheets of blotting paper before testing **[Y. Jin,2002]**.

3.3. Antibacterial properties

The antibacterial properties were quantitatively evaluated against gram negative bacteria, *Escherichia coli* (*E. coli*) and gram positive bacteria *Staphylococcus aureus (S. aureus)*, according to AATCC test method (100-2004). The reduction in numbers of bacteria was calculated using the following equation:

Reduction rate (%) = (A-B)/A*100

Where:

A = the numbers of bacterial colonies recovered from untreated fabrics and

B = the numbers of bacterial colonies recovered from treated fabrics.

3.4. Ultraviolet protection factor (UPF) evaluation

Ultraviolet transmission (UVR) and the ultraviolet protection factor (UPF) was calculated according to the Australian/NewZeland Standard (AS/NZS-4399-1996) as shown in table (1) using UV-Shimadzu 3101-PC-Spectrophotometer.

Table (1): Classifications and grades of UPF

UPF	Classification	Grade
>40	**Excellent protection**	|||
30-40	**Very good**	||
20-29	**Good**		

The following equation which based on the percent ultraviolet radiation transmittance through the specimen used to calculate the UPF.

$$UPF = \frac{\sum\limits_{280\,nm}^{400\,nm} E_\lambda S_\lambda \Delta_\lambda}{\sum\limits_{280\,nm}^{400\,nm} E_\lambda S_\lambda T_\lambda \Delta_\lambda}$$

Where, $E\lambda$ is the relative erythemal spectral effectiveness, $S\lambda$ is solar spectral irradiance in W/cm^2/nm, $T\lambda$ is the spectral transmittance of the fabric (measured), λ is the wavelength in nm and $\Delta\lambda$ is the bandwidth in nm.

3.5. Scanning Electron Microscope (SEM) and Electron Dispersion Emission X-ray (EDX)

SEM was used to obtain photomicrographs of fibers surface morphology by using JEOL-Model JSM-T20 operating at 30 kV. EDX mode was applied for the elemental composition analysis.

3.6. Physico-mechanical properties of fabric
3.6.1. Stiffness

The stiffness of fabrics was determined according to ASTM procedure (D/1388-96- 2002).

3.6.2. Tearing resistance

Resistance to tearing of fabrics was determined by falling pendulum type (Elmendorf) apparatus according to ASTM procedure (D/ 1424-96-2002).

3.6.3. Tensile strength and elongation

The tensile strength and elongation at break were determined according to ASTM procedure (D/3822-01-1997).

3.6.4. Air permeability

The air permeability of the fabric was determined according to ASTM procedure (D/737-04-2008).

3.6.5. Wettability properties

The wettability of untreated and coated fabrics were evaluated according to AATCC test method (79-2007).

3.7. Color strength

The color strength (K/S) of dyed fabrics was measured using Mini Scan^{TM} XE Hunter-lab Universal Software, which based on the kubelka-Munk equation:

$$K/S = (1-R)^2/ 2R$$

Where K = absorption coefficient, S= scattering coefficient, R= fraction of light reflected at a wavelength of maximum absorbance or minimum reflectance **[N. A. Ibrahim,2010]**.

3.8. Fastness properties measurements
3.8.1. Light fastness

The light fastness of dyed fabrics was determined according to ISO test method (105-B02-1999).

3.8.2. Wash fastness
The wash fastness of dyed fabrics was determined according to B.S. test method (2680-1961).

Results and Discussion

4.1. Treatment of wool fabrics by PU and ZnO in single bath
As, the imperative goal in finishing field is to find a degradable replacement chemicals for multifunctional finishing processes, ZnO and PU were used in this research to impart wool fabrics antibacterial as well as wet crease recovery angle **[C. Y. Shih,2003]**. *ZnO* was used for acquiring antibacterial properties while *PU* binder for enhancing wet crease recovery angle of wool fabrics **[Y. L. Lam,2012]**.

4.1.1. Effect of PU concentration on antibacterial activity and wet crease recovery
PU concentration has a direct impact on the wet crease recovery angle and antibacterial effect of the finished wool fabrics. As shown in table (2), when the PU concentrations increased, the wet crease recovery angle and the bacterial reduction (%) increase and reach to the maximum value at 75 g/L, after that both bacterial reduction (%) as well as wet crease recovery angle values were declined at 100 g/L of PU concentration. So the optimum concentration of PU is 75 g/l as the network permit the penetration of ZnO, further increase in PU concentration the network formed decrease the ZnO penetration.

Table (2): Effect of PU concentration on antibacterial activity and wet crease recovery angle

Polyurethane concentration (g/l) (o.w.b)	Bacterial reduction (%)		Wet crease recovery angle (WCRA°)
	S.aureus	*E.coli*	
Blank	**0**	**0**	**245**
25	**51**	**31**	**329**
50	**50**	**50**	**340**
75	<u>**81**</u>	<u>**53**</u>	<u>**353**</u>
100	**74**	**43**	**327**

Finishing Conditions: [ZnO]: 6 g/l (o.w.b), batch temperature: 25 ℃, batch time: 2 hours, cure temperature: 120 ℃, cure time: 3 min, Wet pickup: 100%.

4.1.2. Effect of ZnO concentration on antibacterial activity and wet crease recovery
Table (3) shows the effect of ZnO concentration on antibacterial properties and wet crease recovery of finished wool fabrics. From these results, it was observed that increasing of ZnO concentration accompanied by increasing in both bacterial reduction (%) as well as wet crease recovery angle. As increasing ZnO concentration at 6 g/l, the bacterial reduction (%) reached to 81% and 53% with *S.aureus* and *E.coli* respectively and the wet crease recovery angle reached to 353°. These results may be attributed to the action of Zn^{+2} metal ions which loaded and physically trapped firstly to the fabric, in addition to applying PU binder creating another

layer of protective coating film that in turn increases the wet crease recovery efficiency [**R. M. Kotb,2014**].

Table (3): Effect of ZnO concentration on antibacterial activity and wet crease recovery angle

Zinc oxide concentration (g/l) (o.w.b)	Bacterial reduction (%)		Wet Crease recovery angle (WCRA°)
	S.aureus	*E.coli*	
Blank	**0**	**0**	**245**
1	70	47	321
3	80	50	335
6	<u>81</u>	<u>53</u>	<u>353</u>
9	75	46	306

Finishing Conditions: [PU]: 75 g/l (o.w.b), batch temperature: 25 ℃, batch time: 2 hours, cure temperature: 120 ℃, cure time: 3 min, Wet pickup: 100%

4.1.3. Effect of wash durability on the antibacterial activity and wet crease recovery

Table (4), shows the effect of washing cycles on the properties of finished woolen fabrics. The results revealed that, the wool fabrics which treated with PU only has no antibacterial activity against the both kind of bacteria but it has a distinctly positive effect on the wet crease recovery angle. It enhances the crease from 245° to reach 350° even after twenty wash cycles. PU has an isocyanic group (R—N═C═O) in its chemical structure which can readily react with the amino group of woolen fabrics and form a thin layer on the surface of the fiber. This layer covers the scales of the fibers so they lose the freedom of relative mobility, and on the other hand, this layer forms multispot linkages between fibers, and thus, the wet crease recovery angle of wool fibers improves [**C. Y. Shih,2003**].

On the contrary, the treated wool fabrics with ZnO only have obviously antibacterial activity against the both kind of bacteria but have a slightly effect on the wet crease recovery angle. The possible mechanism for ZnO antibacterial reduction is the release of Zn^{2+} ions. It is well known that ZnO normally becomes unstable in the solution and when H_2O_2 is generated, the Zn^{2+} ion concentration is increased as a result of ZnO decomposition [**A. A. Tayel, 2011**]. Zn^{2+} metal ions are toxic to microbes at very low concentration either in free- state or in compounds. They kill microbes by binding to intracellular proteins, DNA, and lipids damaging them [**R. M. Kotb,2014**]. However, it is washed away after twenty wash cycles which may be attributed to the agglomeration of metal oxide particles (ZnO) that could not enter the space between the fibres and appeared mostly on the fabric surface and hence, washed out easily [**Y. L. Lam,2013**]. While the woolen fabrics treated with PU/ZnO mixture have the best properties of antibacterial activity as well as the wet crease recovery angle which were improved even after twenty wash cycles or in other words they have an excellent

laundering durability. The wet crease recovery angle reached to 356° and the antibacterial activity to 82% and 53% against *S.aureus* and *E.coli* respectively.

As the ZnO is not stably affixed and required a chemical binder, so, the addition of PU dispersion which is self-crosslinking binder assists the chemical and fiber attachment **[Y. L. Lam,2013]**. Therefore, ZnO can be confined in the network structure of the reactive synthetic resin of PU that is formed on the fiber surface **[Y. L. Lam,2012]**. So the antibacterial mechanism in this case attributed to the direct contact between the finished substrate and the microbes or in other words acting as a barrier rather than by the diffusion of the antibacterial agents, so AATCC 100 used in this evaluation **[A. M. Bonilla,2012]**.

The durability of antibacterial activity of finished woolen fabric (PU/ZnO) may be attributed to the chemical bonds between PU functional groups and amino acid of wool macromolecule **[Y. Jin,2002]**.

Table (4) Effect of wash durability on antibacterial activity and wet crease recovery angle

Treatment type	No. of washing cycles								
	0			5			20		
	B.R. %		WCRA°	B.R. %		WCRA°	B.R. %		WCRA°
	S.aureus	*E.coli*		*S.aureus*	*E.coli*		*S.aureus*	*E.coli*	
Blank (untreated)	0	0	298	---	---	245	---	---	212
PU only	0	0	335	0	0	342	0	0	350
PU / ZnO	74	44	338	<u>81</u>	<u>53</u>	<u>353</u>	82	53	356
ZnO only	46	34	323	56	46	325	31	0	324

Finishing Conditions: [PU]: 75 g/l (o.w.b), [ZnO]: 6 g/l (o.w.b), batch temperature: 25 ℃, batch time: 2 hours, cure temperature: 120 ℃, cure time: 3 min, Wet pickup: 100%.

4.1.4. Effect of curing temperature on antibacterial activity and wet crease recovery

The effect of curing temperature on the antibacterial activity of the finished fabric as well as the wet crease recovery angle was shown in table (5). It was found that maximum antibacterial activity was obtained at temperature 110°C where the percentage of bacterial reduction were 89% and 89% for *S.aureus* and *E.coli* and the wet crease recovery angle was 354°. This result may be related to the curing temperature increases more than 100°C, the layer over the fibers becomes more fixed by the heat, and the fibers lose the freedom of relative mobility.

Further increase in the curing temperature up to 130°C the antibacterial activity and wet crease recovery decreased which may be attributed to the higher temperature speeded up the degradation of the bonds between the resin and the fiber [**C. Y. Shih,2003**].

Table (5) Effect of curing temperature on antibacterial activity and wet crease recovery angle

Curing temperature (°C)	Bacterial reduction (%)		Wet crease recovery angle (WCRA°)
	S.aureus	*E.coli*	
Blank	**0**	**0**	**245**
100	**77**	**85**	**344**
110	**<u>89</u>**	**<u>89</u>**	**<u>354</u>**
120	**81**	**53**	**353**
130	**79**	**56**	**338**

Finishing Conditions: [PU]: 75 g/l (o.w.b), [ZnO]: 6 g/l (o.w.b), batch temperature: 25 ℃, batch time: 2 hours, cure time: 3 min, Wet pickup: 100%.

4.1.5. Effect of curing time on antibacterial activity and wet crease recovery
Curing time is considered an important factor that affects on the wet crease recovery angle and antibacterial properties of finished wool fabrics**.** The results in table (6) revealed that the shorter the curing time, the better the wet crease recovery angle and the antibacterial properties. The maximum antibacterial activity against *S.aureus* and *E.coli* were 95% and 92% and 354° of wet crease recovery angle obtained at curing time 2 minute. This effect is presumably a result of the accomplishment of the reaction between the finishing agents and fiber at this short curing time, which promotes the resistance to creases **[C. Y. Shih,2003]**. Further increase in the curing time both antibacterial activity and wet crease recovery decrease which may be attributed to increase time speeded up the degradation of bond to some extent between the PU and fiber surface.

Table (6) Effect of curing time on antibacterial activity and wet crease recovery angle

Curing time (min)	Bacterial reduction (%)		Wet crease recovery angle (WCRA°)
	S.aureus	*E.coli*	
Blank	**0**	**0**	**245**
2	**<u>95</u>**	**<u>92</u>**	**<u>354</u>**
3	**93**	**89**	**354**
4	**91**	**81**	**343**
5	**89**	**80**	**343**

Finishing Conditions: [PU]: 75 g/l (o.w.b), [ZnO]: 6 g/l (o.w.b), batch temperature: 25 ℃, batch time: 2 hours, cure temperature: 110 ℃, Wet pickup: 100%.

4.2. Scanning Electron Microscope (SEM) and Electron Dispersion Emission X-ray (EDX)

The possible changes of the surface morphology of the finished wool fabric under optimum conditions were estimated by SEM and EDX analysis. Wool fabrics finished with PU, ZnO and their mixture were evaluated.

Fig.(3) shows the SEM image of wool samples at a magnification of 3000X. Fig.(3a) showed the SEM image of untreated wool fabric was clean **[M. Mohsin,2014]**, the fiber was rough and scales were sharp **[E. Pooja,2014]**.

By comparing SEM photograph of PU finished wool sample Fig.(3b) with the untreated wool fabric, it was noticed that the surface of the finished wool fabric was coated with a thin transparent layer of PU binder and scales of wool fibers are coated **[H. Yi, 2008].** In addition, the scale edges of treated fibers got blunt slightly and become more smoothness, this result agree with previous one **[E. Pooja,2014]**, **[H. Yi,2008]**.

In case of ZnO treated only Fig.(3c), it was observed that ZnO was deposited on the scale edges of the fibers, and no changes can be demonstrated for the smoothness of fiber surface.

While the SEM of finished wool fabric of PU/ZnO mixture, Fig.(3d) shows the coating of wool fibers with PU, and spreading of ZnO along the fiber as well as covers the sharp scales of wool fiber.

In addition to that, the irregular shaped of ZnO particles can be observed in Fig.(3d) as cluster shape, which are unevenly distributed on the fiber surface or between the fibers also their size are varied. These agglomeration of particles was observed mainly due to the attraction between metal oxide particles on the surface **[Y. L. Lam,2012]**, or may be because it trapped by PU resin Fig.(3d).

Fig.(4) shows the elemental composition analysis of Zn^{2+}. From these results it was observed that Zn^{2+} element concentration was 9.64 wt.% in ZnO treated only as shown in Fig.(4a), but in case of PU/ZnO mixture Fig.(4b) was increased to reach to 20.34 wt.%. This may be attributed to the PU resin polymer which create a coating layer and cover the metal oxide particles, so, the ZnO particles are physically trapped between the fibers **[R. M. Kotb,2014]**. Therefore increase the attachment of ZnO particles to the wool fabrics.
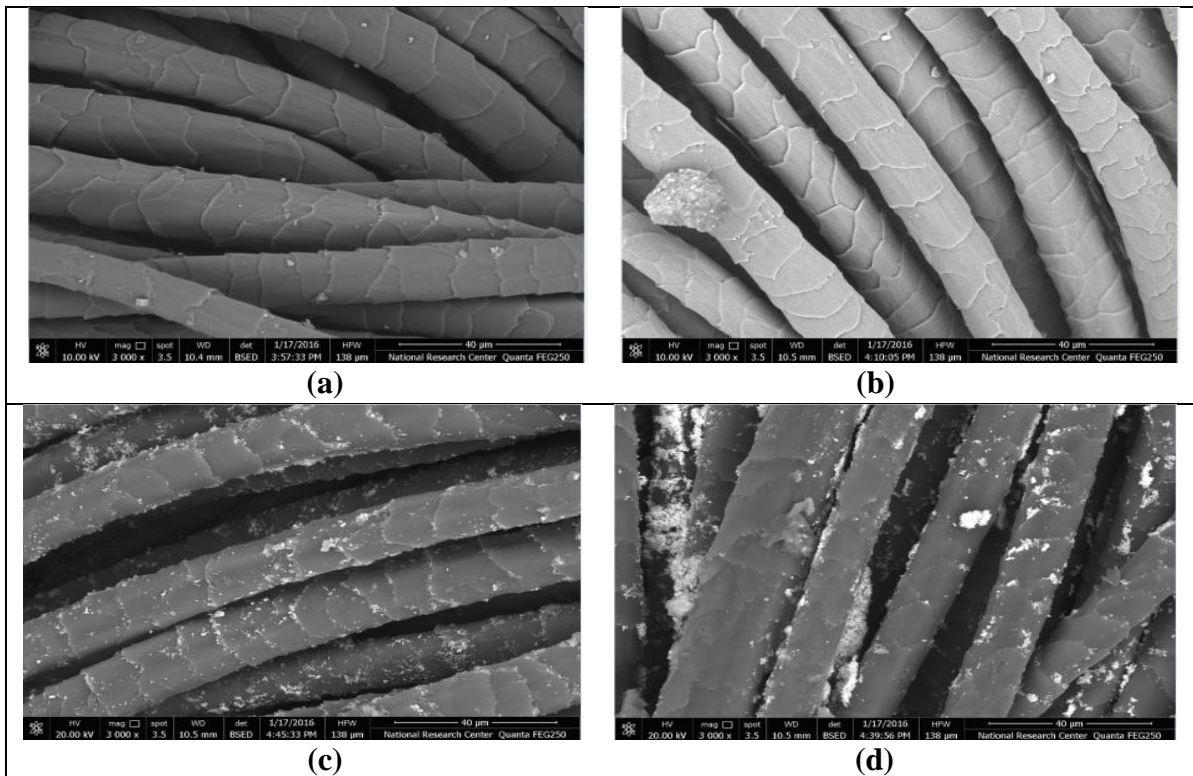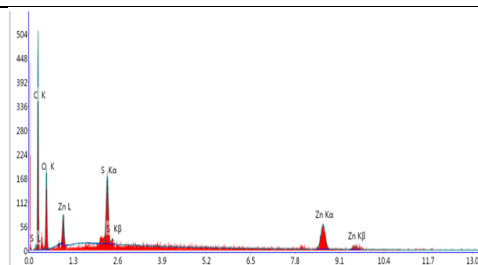
Figure (3): SEM of wool fabrics surface morphology (a) untreated fabric; (b) PU binder coated fabric; (c) ZnO treated fabric; (d) PU with ZnO mixture coated fabric.
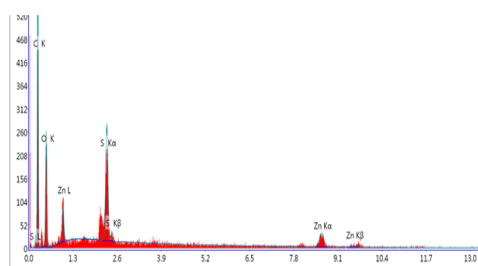
Element	Weight %	Atomic %	Net Int.	Error %
C K	57.88	70.91	20.64	10.33
O K	26.07	23.97	10.89	13.62
S K	6.42	2.95	21.27	5.52
ZnK	9.64	2.17	4.82	15.45

(a)

Element	Weight %	Atomic %	Net Int.	Error %
C K	54.55	72.44	15.66	11
O K	20.23	20.17	7.84	14.25
S K	4.88	2.43	13.75	9.06
ZnK	20.34	4.96	9.27	8.65

(b)

Figure (4): EDX micrographs of wool fabrics (a) ZnO treated fabric, (b) PU with ZnO mixture coated fabric

4.3. Evaluation of ultraviolet Protection Factor (UPF)

UV protection is mainly determined by fiber type and hence chemical composition; fabric construction; additives; textile processing aids; fabric finish and color **[R. M. Kotb,2014],[Y.**

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L. Lam,2011]. It is suggested that UPF of apparel and garment application should be at least 40 to 50+ **[R. M. Kotb,2014]**. The UPF of untreated and finished wool fabrics (after 5,20 wash cycles) was evaluated as shown in table (7).

The UV protection property of the untreated wool fabric showed that the fabric afforded very good protection against UV radiation. The UPF value of the control fabric was 36.91 that may be attributed to its construction.

It was observed that the UPF of wool fabrics finished with PU/ZnO mixture was increased after 5 cycles and reached to 55.25 i.e. excellent UV protection. These results may be attributed to the effect of ZnO particles which were physically trapped and covered the entire fabric surface, so more surface area available for diffuse reflection, scattering, and absorption of UV radiation **[H. Yang,2004]**,**[R. M. Kotb,2014]**.

Furthermore from these data, it was observed that the washing cycles (20 wash) enhanced the UV–blocking efficiency of wool fabrics and give 68.71. This may be due to the reduction in wool fabric porosity associated with shrinkage **[G. Hustvedt,2005]**,**[M. S. Khalilabad,2013]**.

Table (7): Ultraviolet protection factor (UPF) of the blank and the PU/ZnO finished wool fabrics

Treatment Type	Ultraviolet protection factor (UPF)	Classification	Grade
Blank	36.91	Very good	‖
PU/ZnO*	55.25	Excellent	‖‖
PU/ZnO**	68.71	Excellent	‖‖

* After 5 washing cycles   ** After 20 washing cycles

4.4. Physico-mechanical properties

The impact of treatment on both mechanical and physical properties of blank and finished wool fabrics is represented in table (8), From this data it can be concluded that:

• The evident enhancement of tearing strength is due to the existence of PU resin that resists yarn slippage.

• Tensile strength of wool non-significantly changed i.e. wool retain its tensile strength after finishing.

• Wettability of the finished wool fabric enhanced significantly. The time of wettability decrease with percentage 98%. This result is very important in modification of wool fabric so the application of the modified wool increased. It is well known that the polyether PU caused a very high hydrophilicity that will certainly result in a 'molecular/ether bond ladder which may be attributed to the presence of hydrophilic functional groups (-OH) of the soft segement of the polyurethane backbone. Recent studies have reported hydrophilic polyether PU that was prepared by introducing hydrophilic functional groups to the soft-segment of the PU backbone **[O. Kwon,2007]**,**[Q Heng,2010]**.

Table (8): Physico-mechanical properties of blank wool fabric compared with finished wool fabric

Samples	Stiffness (mg/m)	Resistance to tearing (kg)	Tensile strength (kg)	Elongation (%)	Air permeability cm³/s/cm²	Wettability time (sec.)
Blank	**469**	**1800**	**33**	**62**	**322**	**433**
Finished	**570**	**2733**	**32**	**64**	**371**	**8**

Finishing Conditions: [PU]: 75 g/l (o.w.b), [ZnO]: 6 g/l (o.w.b), batch temperature: 25 ℃, batch time: 2 hours, cure temperature: 110 ℃, cure time: 2 min, Wet pickup: 100%

4.5. Effect of dyeing process

In an attempt to optimize the conditions of both finishing and dyeing process to get valuable product characteristics i.e. color strength, antibacterial and wet crease recovery and ultraviolet protection. For this purpose the effect of finishing bath formulation and dyeing properties were studied. It is well known that the ionic bond between the acid dye (sulphonic groups) and amino groups is strong and due to that the color strength (K/S) of blank wool fabric is (16) as shown in Table (9) which revealed the following results:

- The PU finishing decrease the color strength of dyed wool fabrics compared with blank sample because it makes a film on the surface of the fabric, which decrease the reflection from the dye, so the K/S dyed wool fabric after PU finishing decrease and become 15. Also it had a higher (WCRA°) about (354°,347°) in case of finishing before dyeing or after dyeing respectively but there was no antibacterial effect in both strains.

- ZnO had negative effect on the color strength of the dyed wool fabric due to the oxidation reaction happened between the dye and ZnO which leads to decrease in cromophoric or auxochromic groups, so the K/S decrease. Consequently finishing after dyeing led to decrease the color strength more than dyeing after finishing. The order of color strength of dyed fabric as follow in descending order (depending on finishing bath) dyed blank > PU > PU+ZnO > ZnO. Applying finishing after dyeing decrease the color strength of the dyed fabric with percentage 50% whereas dyeing after finishing decrease the K/S 37.55% compared with dyed blank wool fabric. also ZnO only had a high bacterial reduction % about (92,96) in case of finishing before dyeing and (94,97) in case of dyeing before finishing to both *S.aureus and E.coli respectively* and had a slightly effect on (WCRA°) about (320°,303°) in case of finishing before dyeing or after dyeing respectively.

- The highest bacterial reduction % was obtained when using PU/ZnO mixture that about (96,98) in case of finishing before dyeing and (96,97) in case of dyeing before finishing in both *S.aureus and E.coli* respectively. Also it was the highest in (WCRA°) that about (358°,357°) in case of finishing before dyeing or after dyeing respectively.

- The color strength of the fabrics dyed after finishing is higher than those dyed before finishing, this is may be due to that the fabric in the presence of PU causative the increase in affinity between the fabric and the dye stuff that enhances the dye uptake.

- So, the fabrics which finished with PU/ZnO mixture afforded the maximum results for both techniques (finish then dye and dye then finish). However finishing before dyeing was the best.

Table (9): Effect of acid dyeing on color strength (K/S) values, antibacterial and wet crease recovery angle

Technique types	Treatment	Color strength (K/S)	Reduction %		(WCRA°)
			S.aureus	*Ecoli*	
Dye only	Untreated	16	0	0	300
Dyeing after finishing	PU only	15	0	0	354
	PU/ZnO	13	96	98	358
	ZnO only	10	92	96	320
Finishing after dyeing	PU only	15	0	0	347
	PU/ZnO	12	96	97	357
	ZnO only	8	94	97	303

Finishing Conditions: [PU]: 75 g/l (o.w.b), [ZnO]: 6 g/l (o.w.b), batch temperature: 25 ℃, batch time: 2 hours, cure temperature: 110 ℃, cure time: 2 min, Wet pickup: 100%.

Exhaustion dyeing conditions: C.I. Acid Violet 48 dye concentration 2% (owf), Glauber's salt 2g/l (owb), pH (4.5-5), L:R 50:1.

4.6. Fastness properties

Fastness properties including washing and light were carried out for blank dyed wool fabrics and also for finished wool fabrics with PU/ZnO mixture then dyed with C.I. Acid Violet 48.

The data in table (10) showed excellent wash fastness properties of blank dyed wool fabric and slightly change with the finished wool fabric. This may be attributed to that PU act as a binder by making complex between wool with dye. The fastness to light also was slightly change but shows a good light fastness for the blank and finished dyed wool fabrics.

Table (10): Fastness properties of untreated and treated wool fabrics dyed with acid dye

Dye	Wash fastness						Light fastness	
	Color alteration		Staining on wool		Staining on cotton			
Acid Violet 48	Untreated wool fabric	Treated wool fabric	Untreated wool fabric	Treated wool fabric	Untreated wool fabric	Treated wool fabric	Untreated wool fabric	Treated wool fabric
	5	5	4	5	4	5	3	4

Conclusion

Mixture of PU/ZnO was found to be multifunctional finishing of woolen fabric in enhancement the wettability, antibacterial finishing, wet crease recovery as well as the UV protection using pad-batch –cure technique. In terms of the antibacterial properties and wet crease recovery, the results showed that a concentration of a mixture of PU/ZnO using 75g/l PU (o.w.b) and 6 g/l ZnO (o.w.b) was sufficient to impart excellent antibacterial properties to wool fabric against *S.aureus* and *E. coli* about 95%, 92% respectively, and impart excellent

wet crease recovery about 354°. The results obtained from SEM and EDX analysis showed changing in surface morphology of coated fabrics. The treatment gave a UPF value of 55.25, which mean it has excellent UV protection category. The PU/ZnO coated fabric preserved excellent durability in regard to antibacterial activity, wet crease recovery and UV protection, even after twenty cycles of washing. Physico-mechanical properties including stiffness, tearing strength, elongation, air permeability and wettability properties was increased but tensile strength unchanged. The acid dye type; C.I. Acid Violet 48 was used through different approaches. The best result in color strength, antibacterial and wet crease recovery obtained in case of carrying out the dyeing after finishing. Likewise, both wash and light fastness properties have a slightly change.

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