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Synergizing effect of poly quaternary ammonium salts and metal oxides nanoparticles on wool and wool/polyester fabrics

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A new finishing technique using quaternary ammonium groups (QAG) via polymerization of methacryloyloxyethyl ammonium chloride (PMAETAC), in presence of TiO_2 /ZnO / TiO_2+ZnO nanoparticles in wool, wool/polyester fabrics has been studied, using $K_2S_2O_8$ as initiator for the graft copolymerization reaction. The antimicrobial activities of the finished fabrics have been assessed against *Staphylococcus aureus*, *Escherichia coli and Pseudomonas aeruginosa* as well as *Candida albicans*. The findings show that, the finished fabrics with PMAETAC and their hydride combination with metal oxide NPs have outstanding activity against *E. coli* & *S. aureus* as well as excellent UV protection as compared to that finished with PMAETAC alone. The finished fabrics are also characterized by Fourier transformation infrared. The topography of the fabrics surface is examined by SEM and EDX. After five washing cycles, the acquired properties are found slightly affected, indicating an excellent wash durability.

Keywords: Antimicrobial, Cationic polymer, Metal oxides NPs, Ultraviolet protection factor, Wool

1 Introduction

Natural clothing textiles are considered as media for the growth of the pathogenic bacteria and mildew causing biodegradation of the clothing and the transfer of a microbes. This leads to an increased demand for the antimicrobial protection. Extensive studies were carried out on the durable antimicrobial finishing of woolen fabrics with concentricity on durable microbial activity [1-3].

Wool keratin is made of 18 amino acids, containing amino, carboxylic and amide groups as well. They are the main reactive sites for woollen polymer interactions. Free amino groups of protein could form cationic amino groups in acidic medium, consequently interact with anionic groups' through ionic linkages. Similarly, carboxylic acid groups could form carboxylate anions through ionic linkages with cationic agents. This approach is similar to the recent approach, reporting antimicrobial modifications of acrylic and nylon fabrics[4-6]. Antimicrobial finishing in the textiles is essentially required in recent years, as a result of increase in pathogenic effect of microorganisms on various textile products, such as durable medical textiles.

One of the most common antimicrobial agents is the quaternary ammonium salts (QAS) which destroy the cell membrane of microbe. It is well known that, QA salts are used for textile disinfection[7]. Monomeric quaternary ammonium compounds have higher efficiency due to their leash with the polymer. Combinations of dially groups and QAS will enhance the microbial resistance as well as extend the application scope. It was reported that novel QAS, which includes both diallyl and perfuloroalkyl, is favorable finishing agent for imparting the fabrics with antimicrobial properties as well as resistance to oil, soil and water[8].

Poly(methacryloyloxy) ethyl trimethyl ammonium chloride (PMAETAC) is a cationic polymer, consisting of quaternary ammonium groups[9]. Cotton fabric grafted with PMAETAC exhibited antimicrobial activities against Gram-positive and Gram-negative bacteria. The activity was found to increase with increasing the grafting yield of the polymer[10]. Woolen fabric modified with conjugate materials from chitosan and PMAETAC, showed antimicrobial activity. It is worth mentioning here that the polymers with antimicrobial activities have gained significant attention due to their numerous characteristics benefits, such as prolonged term efficiency, low toxicity, non permeability through skin and chemical stability[10]. It is well known that

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most of heavy metals are toxic to microbe at low concentrations (either in compounds or in free state) through interacting with intracellular proteins, consequently deactivating the microbes. Nano-metal oxides such as titania TiO_2 and zinc oxide ZnO have recently emerged as new biocides.

The present work is therefore undertaken to impart multifunctional properties, such as antimicrobial activity and protection against ultraviolet radiation, on wool and wool/polyester fabrics through the synergetic effect of vinyl quaternary ammonium compound (methacryloyloxy ethyltrimethyl ammonium chloride) and metal oxides nanoparticles (NPs), such as TiO_2, ZnO and TiO_2+ ZnO. PMAETAC/ NPs metal oxides were prepared by the polymerization of MAETAC in the presence of TiO_2, ZnO and their hybrid mixture. The NPs metal oxide could disperse inside the grafted polymer layer(s), which could enhance the extent of fixation of the finishing agents as well as its durability. The antimicrobial properties of the modified fabrics before and after washing have also been investigated along with their ultraviolet protection.

2 Materials and Methods

2.1 Materials

Mill scoured 100% wool fabric (count warp + weft 32 ends/cm & 20 picks/cm, and weight 268 g/m^2) and 40/ 60 wool/polyester blend (count warp + weft 45 ends/cm & 50 picks/cm and weight 220 g/m^2) were used. Vinyl quaternary ammonium salt (methacryloyloxye thyltrimethyl ammonium chloride) (MAETAC) aqueous solution (65%), TiO_2 & ZnO nano-powder (Sigma-Aldrich) and potassium persulphate ($K_2S_2O_8$), analytical grade, were used. The antimicrobial potential of finished fabrics was tested using one Gram-positive bacteria (*Staphylococcus aureus* NRRL B-767), two Gram-negative bacteria (*Escherichia coli* ATCC 25955 and *Pseudomonas aeruginosa* ATCC 10145) and one yeast (*Candida albicans* ATCC 10231). Bacterial and yeast strains were cultured overnight at 30±2°C in nutrient broth (NB) and potato dextrose broth (PDB) respectively. These cultures were used as inoculums in antimicrobial test.

2.2 Antimicrobial Assay

2.2.1 Turbidity Method

The antimicrobial activity of finished fabrics was determined by turbidity method[11, 12]. Briefly, 30 µL of the tested microorganism [10^6 colony-forming units (CFU)/mL] was inoculated into 3 mL of nutrient broth (NB) or potato dextrose broth (PDB) medium in standard test tubes containing the sample (2×2cm^2). Test tubes were incubated at 30±2°C for 24h under shaking conditions. Antimicrobial activity was evaluated by measuring the optical density (OD) at 600 nm and compared to the blank sample.

2.2.2 AATCC TM 100 Method

The antimicrobial activity of finished fabrics was determined according to AATCC TM100 method[13], with some modifications. Samples (1×1 cm^2) were placed in sterilized glass tubes and moistened with 100 µL sterile phosphate buffer. Overnight grown tested cultures (30µL) were used for inoculation of the fibre and then it was incubated at 30°C for 24h. Ten fold serial dilutions of each sample were spread onto nutrient agar (three replicates per dilution) and incubated at 30±2°C for 24 h. Microbial colonies grown on these plates were counted and compared with the control sample (blank). The reduction percentage was calculated using the following equation.

$$\text{Reduction percentage} = [(A\text{-}B)/A)] \times 100$$

where A and B are the OD at 600 or the number of colony forming units of blank and treated samples respectively. The data was the mean of three replicas.

2.3 Finishing

2.3.1 Finishing of Fabrics with MAETAC

Wool and wool/polyester fabrics (20×20 cm^2) were padded at room temperature (25 ◦C) in a completely soluble solution of MAETAC (10 %) and potassium persulphate (2 g/L). The fabrics were then removed from the bath, squeezed to a suitable pick-up % using a laboratory padder (ROACHES, UK), and then dried at 80°C for 3 min in an oven (ROACHES, UK), followed by curing at 120°C for 5 min. The dried samples were washed five times with hot water to remove the homo-polymer of PMAETAC. The finished fabrics were dried in an oven at 80°C for 2h. In order to evaluate the efficiency of the fabrics finishing, the fabrics were repeatedly washed for five cycles according to the standard AATCC test method 61-1989 (ref. 14).

2.3.2 Finishing of Fabrics with MAETAC and Metal Oxide NPs

Finishing of wool and wool/polyester fabrics was carried out as per the abovementioned method with

addition of 1 g/L TiO_2, ZnO NPs and their mixture (1:1 wt/wt).

2.4 Analysis

2.4.1 SEM and EDX Analysis

Spectra of selected finished fabric samples were investigated using a JEOL-Model JSM T20 equipped with X-ray spectroscopy to clarify the changes in surface morphology and to confirm the presence of elements onto the surface of the tested samples.

2.4.2 FTIR Analysis

The chemical structure was determined using the Fourier transformation infrared (FTIR) spectrometer (model NEXUS 670, NICOLET USA). The measurements were carried in spectral range 500-4000 cm^{-1}. Reflection percentage measurement technique was applied (R %) to all investigated samples.

2.4.3 UPF Factor

UV-protection factor (UPF) of functionalized woolen containing fabrics was assessed according to AATCC Test Method 183:2010 UPF using UV-JASCO V-750 spectrophotometer.

3 Results and Discussion

3.1 Effect of Finishing on Antimicrobial Properties

Efforts have been made to acquire new properties, such as antimicrobial as well as ultraviolet protection on wool and wool/polyester fabrics via synergizing poly-quaternary ammonium vinyl monomer and metal oxide NPs. The reduction percentage test has been used to investigate the microbial reduction quantitatively. Table 1 shows the effect of finishing of fabrics with PMAETAC and TiO_2/ ZnO/ TiO2+ZnO (1:1) NPs on their antimicrobial activities. The results show that the fabrics finished with PMAETAC acquire antimicrobial activities, which may be due to the nature of cationic polymer. The exact action mechanism of quaternary ammonium compounds has not been completely explained yet, but the dominant action usually causes breaking of the cell membrane[9]. The antimicrobial efficiency is obtained from the positively charged nitrogen atoms of quaternary ammonium groups, which are hound to adhere (come into contact) with microbes through the negatively charged microbial cell membrane, leading to perturbation in balance of electrical charges and its lysis.[7]. Another assumption suggests that the antimicrobial activity of the QAS assumes the reaction between lipids and proteins of the cell membrane, which leads to disorganization in its structure and the leakage of low-molecular components out of the cell. Then, proteins and nucleic acids degrade inside the cell. The release of autolytic enzymes leads to the lysis of the cell wall components. These processes cause complete loss of the structural organization of the cell[9]. As shown in Table 1, the antimicrobial activities of PMAETAC vary with the changes in types of microbe. This agrees with the other reported findings stating that the QASs have different biological activity against Gram-positive and Gram-negative bacteria[15].

The activity of the PMAETAC +TiO_2 NPs mixture is slightly decreased as compared to that finished with PMAETAC alone. This may be due to the interaction between both of them through hydrogen bonds and electrostatic forces[16].

Table 1 shows that the wool fabric displays higher activity as compared to wool/polyester blend fabrics, in case of finishing with the polymer alone. This may be resulted from higher interaction between wool reactive sites in pure fabric than in blended one. It is expected that TiO_2, ZnO and

Table 1 — Effect of finishing on antimicrobial activities of wool and wool/polyester fabrics

Fabric	Finishing bath formulation	Reduction percentage			
		E. coli (Gram –ve)	*P. aeruginosa* (Gram –ve)	*S. aureus* (Gram +ve)	*C. albicans* (Yeast)
Wool	PMAETAC	85.3	89.0	95.0	85.1
	PMAETAC +TiO_2	81.0	72.4	81.0	61.1
	PMAETAC + ZnO	83.3	85.5	92.0	60.0
	PMAETAC+ (TiO_2+ZnO)	90.4	81.0	99.0	73.0
Wool/Polyester	PMAETAC	70.0	50.1	74.0	44.0
	PMAETAC +TiO_2	69.0	60.0	76.1	66.1
	PMAETAC+ ZnO	89.6	90.0	93.5	83.1
	PMAETAC+ (TiO_2+ZnO)	86.3	75.7	98.7	69.8

Table 2—Effect of washing on antimicrobial activities of wool and wool/polyester fabrics

Fabric	Finishing bath formulation	Reduction percentage							
		E. coli (Gram –ve)		*P.aeruginosa* (Gram- ve)		*S. aureus* (Gram +ve)		*C. lbicans* (Yeast)	
		1 wash	5 wash	1 wash	5 wash	1 wash	5 wash	1 wash	5 wash
Wool	PMAETAC+ (TiO_2+ZnO)	89.0	88.5	80.0	79.0	98.3	97.0	72.0	70.0
Wool/Polyester	PMAETAC+ (TiO_2+ZnO)	85.0	83.8	74.7	73.0	97.9	96.0	68.8	67.2

Table 3 — Effect of finishing on protective properties of wool and wool/polyester against ultraviolet radiation

Finishing formulation	Wool		Wool/Polyester	
	UPF	Rating	UPF	Rating
Nil	95.2	Excellent	19.4	Poor
PMAETAC	99.5	Excellent	31.8	Very Good
PMAETAC +TiO_2	251.0	Excellent	66.2	Excellent
PMAETAC + ZnO	416.0	Excellent	95.3	Excellent
PMAETAC+(TiO_2+ZnO)	629.0	Excellent	97.2	Excellent

TiO_2+ ZnO (1:1) NPs are dispersed within the polymer matrix and the cationic groups of the polymer react with the fabric reactive sites and metal oxide NPs as well. The polymers in nano-composite form [achieved by combining a polymer (or monomer) with dissimilar nano-sized material] can effectively inhibit the combining process of the nanoparticle and retain nanoparticles in a polymer solution well dispersed. The interaction of the surface does not seem to alter a nanoparticles structure. The polymers greatly improve the stability and compatibility of the composite particle dispersion in a polymer matrix, making it easier to apply nanoparticles in many fields[17]. Table 1 reveals that the fabrics finished with cationic polymer and mixture of NPs, exhibit higher antimicrobial activity in comparison with that finished with other formulation. This could be attributed to the reaction of cationic reactive sites of PMAETAC with carboxylic groups and/ or hydroxyl and/or amino groups of the wool fabric, in addition to the reaction of metal oxides NPs with the fabric reactive sites, this enhances the antimicrobial activities of the finished fabrics[17]. It is reported that, the ZnO NPs split the cell membrane of *E. coli* & *P. aeruginosa* (Gram- negative), and release zinc ions which lead to damage of mitochondria and death of bacteria[8,18].

Table 1 reveals that the antibacterial efficiency is higher in case of *S. aureus* than in the case of *E. coli* and *P. aeruginosa* for both types of fabrics[18]. The optimum condition has been obtained in case of polymer + NPs mixture, where the reduction % obtained against *S. aureus* and *E. coli* for wool is 99.0% and 90.0% respectively. For wool/polyester fabric, the reduction % is 98.7 for *S. aureus* followed by 86.0 for *E. coli.*

Table 4 — Effect of washing on protective properties of wool and woo/polyester against ultraviolet radiation for PMAETAC+ (TiO_2+ZnO) finishing

Fabric	1Wash		5 Wash	
	UPF	Rating	UPF	Rating
Woolen	+50	Excellent	+50	Excellent
Wool/polyester	+50	Excellent	+50	Excellent

Table 2 shows that finishing of wool fabrics with PMAETAC and mixture of TiO_2+ ZnO NPs (1:1) enhances the antimicrobial properties even after five standard washing cycles. The antimicrobial activities of wool fabrics are slightly affected, indicating excellent washing durability.

3.2 Effect of Finishing on Protective Properties against Ultraviolet Radiation

TiO_2 and ZnO NPs have excellent UV-shielding characteristic, which indicates that they are useful in industrial textile applications[19]. Table 3 illustrates that the wool fabric exhibits excellent UV protection, due to the surface morphology. It is noticed that, finishing with poly quaternary polymer enhances the UV protection of wool/polyester fabric. This may be due to coating on surfaces with the polymer layer, as the UPF increased from (19.4) to (31). Addition of TiO_2 or ZnO NPs or their mixture to the finishing bath formulation leads to remarkable improvement of UV protection. The enhancement of UPF of the finished fabrics could be arranged in the following descending order:

PMAETAC + (ZnO+TiO_2) NPs > PMAETAC + ZnO NPs > PMAETAC +TiO_2> PMAETAC.

The data listed in Table 4 show that, finishing of wool containing fabrics with finishing bath formulation contains PMAETAC and mixture of TiO_2+ ZnO NPs (1:1) enhance the ultraviolet resistance even after five standard washing cycles.

3.3 FTIR Analysis

Functional groups of wool based fabrics surfaces before and after finishing with PMAETAC alone and (PMAETAC+TiO_2 NPs), (PMAETAC + ZnO NPs) and [PMAETAC+ (TiO_2+ZnO) NPs (1:1)] have been investigated using FTIR spectral analysis (Fig. 1). The IR spectrum of wool has various distinctive absorption peaks, such as the absorption bands at 3000–3900 cm^{-1} assign to stretching vibration modes of OH groups, the absorption band at 2300 cm^{-1} of O-H stretching associated to carboxylic groups of amino acids of polypeptide chains, the absorption band at 1053 cm^{-1} related to -C-O and –C-O-C stretching modes, and the band at 1610 assigned to amide I. The spectra show a new band at ~ 480 -547 cm^{-1}, which could be attributed to Ti−O band of titania, for wool finished with PMAETAC +TiO_2, and PMAETAC + (TiO_2 +ZnO). The bands at ~ 692, 586 and 539 cm^{-1} could be attributed to the Zn-O vibration modes, for wool finished with PMAETAC +ZnO, PMAETAC + (TiO_2 +ZnO). On the other hand, spectra show a slight change in the bands of υ (–C-H_3), υ (–C-H_2), υ(C=O). The bands of amide I (C=O stretching) are shifted from 1688 to 1680, 1685, 1683 cm^{-1} in case of finishing with TiO_2, ZnO and their mixture respectively. The band of amide II (N−H bending) at 1573 cm^{-1} is found shifted to 1567, 1563, and 1566 cm^{-1} in case of finishing with TiO_2, ZnO and their mixture respectively. The bands of amide III (C−N stretching) are shifted from 1242 cm^{-1} to 1240, 1236, and 1243 cm^{-1} in case of finishing with TiO_2 and ZnO and their mixture respectively. Also, the band at 948 $cm^{-1}$of C−O stretching is shifted towards 952, 945, and 939 cm^{-1} in case of finishing with TiO_2 /ZnO and their mixture respectively. So, it could be concluded that metal oxide NPs are coated on the wool by chemical method. The intensities ratio of the bands of amide I and amide II decrease from 5.9 to 2.9, 2.4, and 3.9 for finishing bath formulation containing TiO_2, ZnO, and their mixture respectively. Such decrease in band intensity may be due to bonding of the amide groups to the metallic ions[20–22].

3.4 SEM Studies

SEM topography of finished wool based fabrics with PMAETAC only and (PMAETAC +TiO_2 NPs), (PMAETA$_C$ + ZnO NPs) and [PMAETAC + (TiO_2 +ZnO) NPs 1:1] is presented in Figs 2 and 3. It is observed that the surface of finished fabric with PMAETAC only is smooth and clean. However, there are significant changes, noticed on the fabric surfaces for the finished wool and its blend with polyester using (PMAETAC + TiO_2 NPs), (PMAETAC + ZnO NPs) and [PMAETAC + (TiO_2 +ZnO NPs) 1:1]. The dispersed particles are appeared on the surface, which indicates the loading of TiO_2 NPs, ZnO and their mixture (1:1). Also it is noticed that, the deposition of ZnO NPs is greater than that of TiO_2, which may be resulted from the interaction between TiO_2 NPs and PMAETAC. In addition, EDX analysis is performed for determination of chemical composition, which proves the presence of TiO_2 NPs and ZnO NPs on wool surface, indicating the presence of Ti and Zn on the surface, proving the successful coating process.

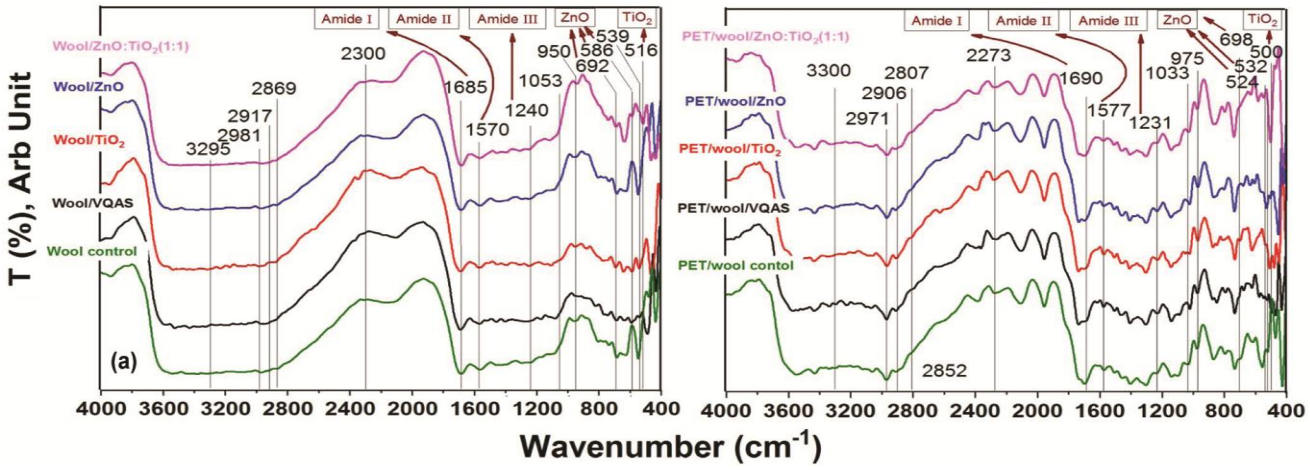

Fig. 1 — FTIR of (a) wool and (b) wool/polyester fabrics

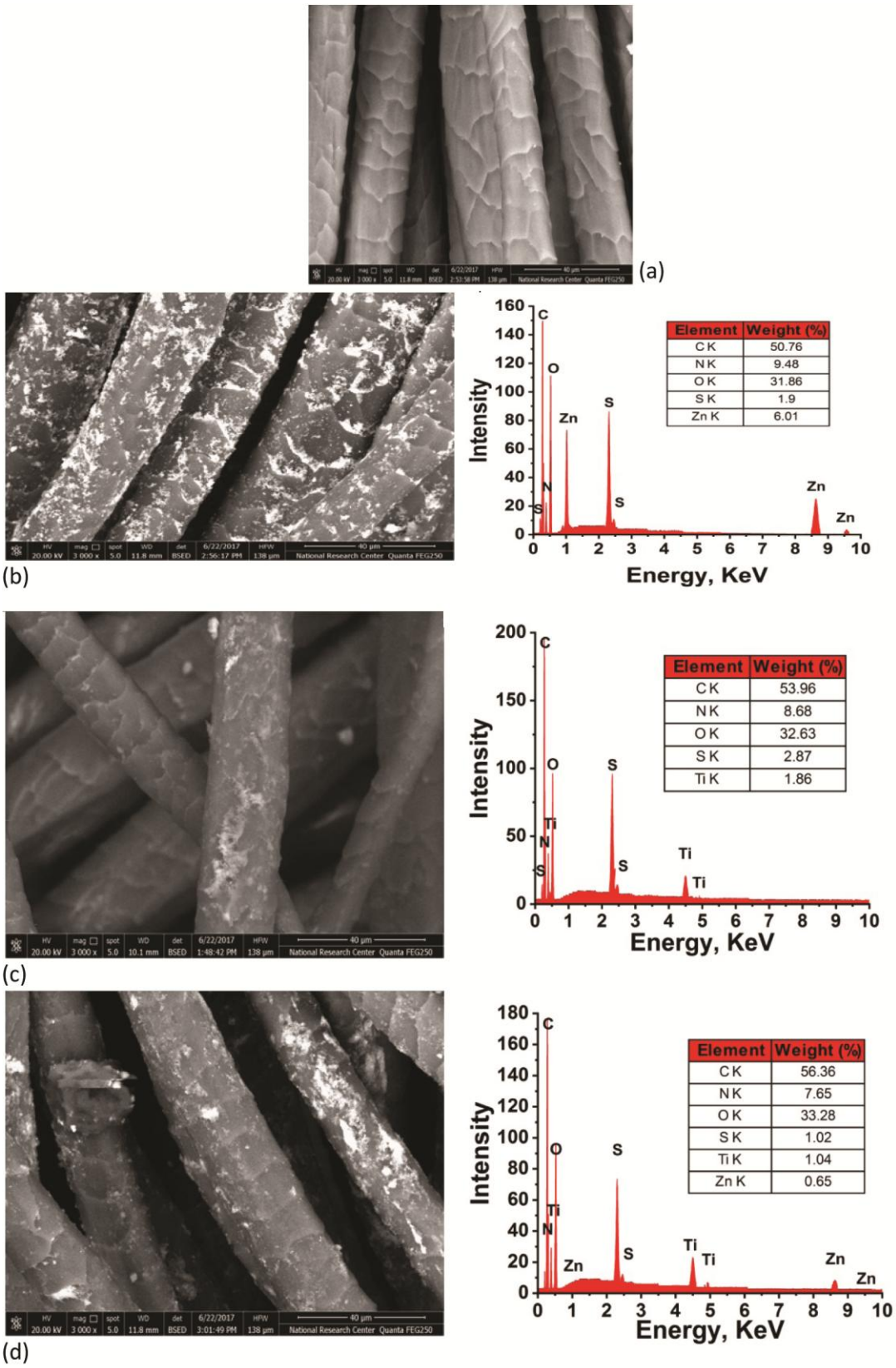

Fig. 2 — SEM images (×3000) of wool fabric finished with (a) PMAETAC, (b) PMAETAC +TiO_2 NPs, (c) PMAETAC + ZnO NPs and (d) PMAETAC + (TiO_2+ZnO) NPs

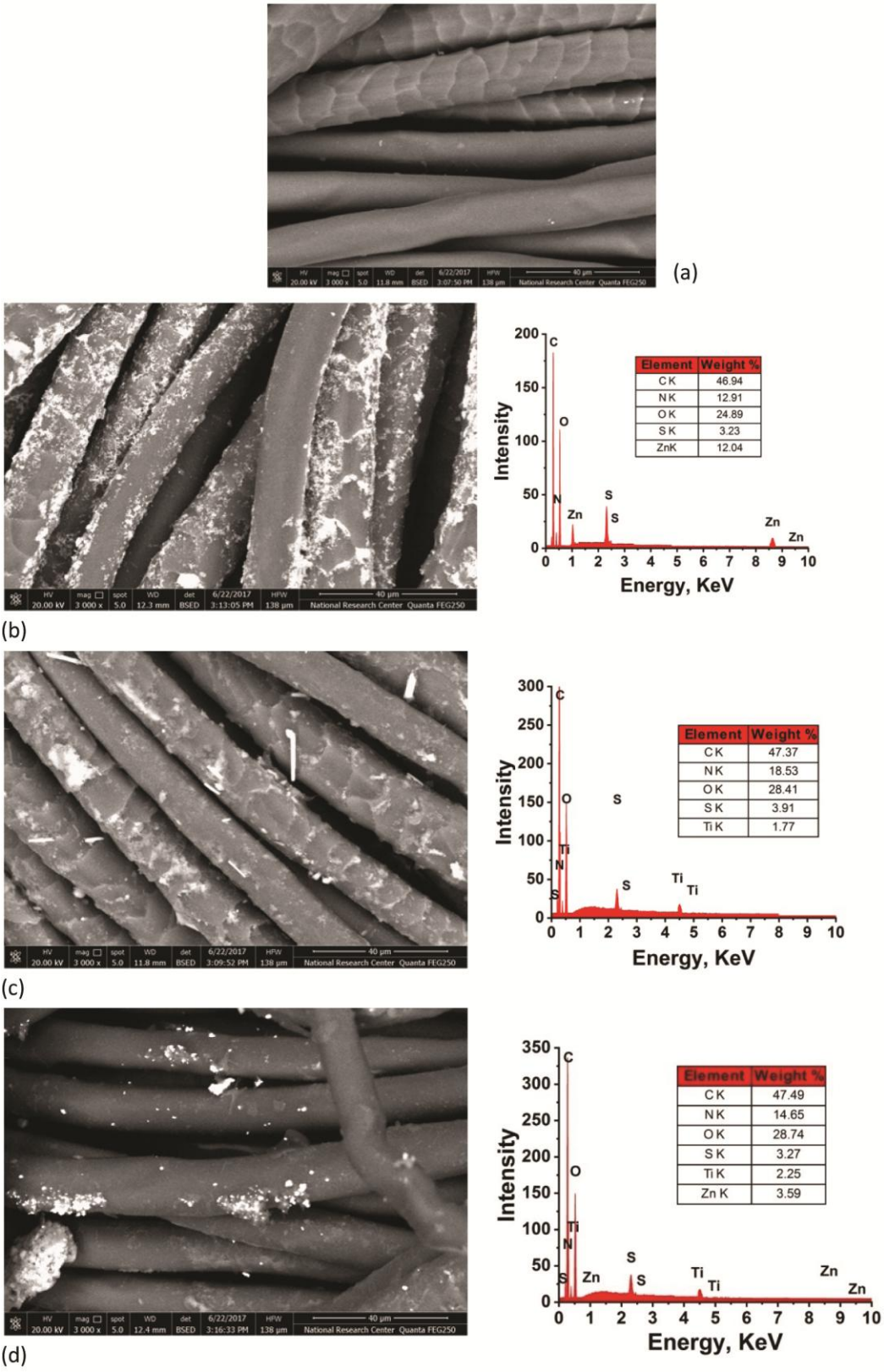

Fig. 3 — SEM images (×3000) of wool/polyester fabric finished with (a) PMAETAC, (b) PMAETAC +TiO_2 NPs, (c) PMAETAC + ZnONPs, and (d) PMAETAC + (TiO_2+ZnO) NPs

4 Conclusion

A new finishing technique has been studied for inclusion of quaternary ammonium groups via polymerization of methacryloyloxyethyl ammonium chloride (PMAETAC), in the presence of TiO_2, ZnO NPs and their mixtures, in wool containing fabrics. It is found that, the finished fabrics with PMAETAC and their hydride combination with NPs metal oxide shows outstanding activity against *E. coli & S. aureus* as well as excellent UV protection. After five washing cycles, the acquired properties are slightly affected, indicating excellent washing durability. The enhancement of UPF of the finished fabrics could be arranged in following descending order:

[PMAETAC + (ZnO+TiO_2NPs)] > (PMAETAC + ZnO NPs) > (PMAETAC +TiO_2 NPs) > PMAETAC.

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