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Modification of viscose fabrics to impart permanent antimicrobial activity

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Viscose fabrics have been modified to enhance the attraction for nano metal oxides, namely aluminum oxide, zinc oxide or titanium (IV) oxide, to impart antimicrobial activity against *Escherichia coli* and *Candida albicans*. Viscose fabrics are pretreated with 3-bromoprpionic acid prior to loading with nano metal oxides. Optimization of the acid concentration is reported. The overall results show a unique ability to stop microorganisms growth on the viscose fabrics pretreated with 3-bromopropionic acid and after treatment with nano metal oxides. The ability of nano metal oxide treated viscose fabrics to reduce the microbial growth is found in the following order: zinc oxide > aluminum oxide > titanium (IV) oxide. The durability of antimicrobial activity has been tested after thirty wash cycles.

Keywords: Antimicrobial activity, Nano aluminum oxide, Nano titanium oxide, Nano zinc oxide, Viscose fabrics

1 Introduction

Textiles can provide a suitable substrate to grow microorganisms especially at appropriate humidity and temperature in contact with human body. Recently, increasing public concern about hygiene has been driving many investigations on antimicrobial agents for textiles. These agents are used to prevent serious undesirable effects on textile materials, such as degradation of coloring, staining and deterioration of the fibers[1-3], formation of unpleasant odor[4], as well as increase of potential health risks[5,6]. A proposal of hygienic living standard by controlling the microorganisms is necessary. Researchers have focused on the antibacterial and antifungal modifications of textiles[7-17]; by application of inorganic nanotechnology[18-26].

As most textile fabrics would undergo repeated laundering during their lifetime, the washing durability of nano metal treated fabric is of significant importance. Polycarboxylic acids are a multi-functional organic molecules with chemical and thermal stability[27,28]. Polycarboxylic acids could form ester linkage with hydroxyl groups of cellulosic fabrics at elevated temperature above 160 °C (ref. 29). They have also been used to improve the adhesion of the inorganic-organic interface[30].

The present work is aimed at preparing permanent antimicrobial viscose fabrics by fixation of propionic acid groups at lower temperature (below 100 °C), as active centers, onto the cellulosic polymeric chain. The added carboxylic groups are believed to act as favorable centers for some oxides such as titanium oxide, zinc oxide or aluminum oxide nano particles. The efficiency of the antimicrobial activity, considering the permanent performance against selected microorganisms onto modified textile, is also evaluated.

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2 Materials and Methods

Plain weave scoured 100 % viscose fabric, procured from Abou El-Ola for Spinning and Weaving, 10[th] of Ramadan, Egypt, was used. The fabric weight is 110 g/m^2, number of warps is 375 /10 cm and number of wefts is 320 /10 cm.

3-Bromopropionic acid (97%) procured from Alfa Aesar GmbH & Co KG Germany, aluminum oxide nanopowder (particle size 50 nm), zinc oxide nanopowder (particle size 50 nm) and titanium (IV) oxide nanopowder (particle size 70 nm) procured from Aldrich, Austria were used. All other chemicals were of laboratory grade and used without any further purification.

2.1 Procedures

2.1.1 Pretreatment of Viscose Fabric with 3-Bromopropionic Acid

3-Bromopropionic acid solution was initially neutralized with sodium carbonate solution to *p*H 7. The viscose fabric was treated with different concentrations of the neutralized sodium

3-bromopropionate (0.2- 3.0 %) solution through padding technique (pickup 80 %), followed by drying at 80 °C for 5 min. The treated fabrics were padded again with 0.5 % sodium hydroxide solution (pickup 80%) and dried at 60 °C for 15 min. The viscose fabric was thoroughly rinsed with water several times, neutralized with dilute hydrochloric acid solution, rinsed again with water, squeezed and dried.

2.1.2 Treatment with Metal Nanopowder

Aluminum oxide, zinc oxide or titanium (IV) oxide nano powder suspensions (0.4 g/l) were sonicated for 30 min. The untreated as well as pretreated viscose fabrics with 3-bromopropionic acid were immersed in the aqueous nanopowder suspension for 10 min, then padded (pickup 80%) and annealed at 75 °C for 60 min. Finally, the samples, loaded with the nanopowder, were washed in ultrasonic bath in distilled water for 5 min to remove unbonded nanopowder[31].

2.2 Measurements

2.2.1 FTIR Study

Samples of untreated viscose fabric, viscose fabric pretreated with 3-bromopropionic acid and finally viscose fabric pretreated with 3-bromopropionic acid and treated with nanopowder were analyzed by FTIR spectrometer, using a Nicolet 60 SXR Fourier transform infrared spectrometer in the attenuated total reflection mode with a KRS5 crystal.

2.2.2 TEM Study

The untreated as well as the pretreated and post treated viscose fabrics with nanopowder were investigated using transmission electron microscopy JEM -1230 JEOL Co. Japan, with 30 KV.

2.2.3 Antibacterial and Antifungal Activities

E. coli sero type O157:H7 was isolated from lambs (young sheep of 12 months of age). *C. albicans* strain was isolated from bovine milk samples as the animal suffered from mastitis.

All tests were conducted by standard plate count technique. All viscose fabrics were prepared at a diameter of 4.8 ± 0.1 cm in plastic bags and then sterilized by autoclaving at 121°C for 15 min. The antibacterial and antifungal properties of untreated viscose fabric, viscose fabric pretreated with 3-bromopropionic acid and/or with nano metal oxides were quantitatively evaluated by using plate count agar method according to the AATCC test method 100–2004. The species of microorganisms used in this experiment were *E. coli.* and *C. albicans*.

Both microorganisms were individually inoculated into tubes containing 5 mL BHI (brain heart infusion broth) sterile suspension. Such suspension was adjusted to 0.5 McFarland standards to match the turbidity of 1.5×10^{-8} mL^{-1} colony forming unit (CFU)[32].

All viscose fabrics were kept at controlled temperature of 35°C. After incubation the viscose fabrics were transferred into 100 ml of nutrient broth (1:500) and shaken vigorously for 1 min. A 10-fold dilution with 0.9 % (w/v) normal saline solution was prepared, spread at varying dilutions onto plates containing EMB for *E. coli* and sabouraud dextrose agar for *C. albicans*. Incubation to all plates was done at 35°C for 24 h.

All experiments were performed in triplicate. The antimicrobial activity is expressed in % reduction of the organisms after making contact with the test specimen compared to the number of the organism cells surviving after making contact with the control. All results were expressed according to the following equation:

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

where *A* is the number of microorganisms present on untreated viscose fabrics; and *B*, the number of microorganisms present on treated viscose fabrics

2.2.4 Wash Fastness

The washing durability test method for the antibacterial treated fabrics was assessed according to the AATCC test method 61–2003. Washing was performed using a laundering machine at 49°C in a stainless steel lever lock container. The fabrics were leached in 0.15 % aqueous solution of sodium lauryl sulfate detergent and in presence of 50 steel balls for 45 min. The samples were rinsed intensively with water and dried at room temperature prior to further investigations.

2.2.5 Elution of Metalized Viscose Samples

Around 2-3 g of the nano metal treated viscose fabrics were treated with 80-90 mL of 0.5 N HCl at 95°C for 20 min. The amounts of the eluted metal ion were measured using atomic absorption spectrometer (VARIAN AA220).

3 Results and Discussion

3.1 FTIR Study

FTIR spectra of untreated viscose fabric as well as treated with 3-bromopropionic acid and nano metals are illustrated in Fig. 1 The spectral features of untreated viscose reveal that it is clearly distinguished by its broad distinguished peak of the hydroxyl groups at 3396.6 cm^{-1} [Fig. 1(a)]. Formation of a new peak is observed, at 1560 cm^{-1} upon the treatment of viscose fabric with 3-bromopropionic acid [Fig. 1(b)]. This is a charactristic peak of the stretching vibration band of carboxylate groups introduced to the fabric surface. This new peak can be taken as support for the reaction mechanism between the viscose fabrics and 3-bromopropionic acid (Fig. 2). Spectral features of viscose fabrics pretreated with 3-bromopropionic acid and after treated with nano metal oxides (Ti, Al or Zn) are characterized by no change in comparison with that of viscose treated with 3-bromopropionic acid only [Fig. 1(c-e)].

3.2 Alkali Combining Capacity of Viscose Fabric

Figure 3 shows the relation between the concentration of 3-bromopropionic acid used in pretreatment and the value of alkali combining capacity (carboxyl content) of the modified viscose fabrics. The data reveal that, the untreated viscose fabric has a moderate amount of carboxyl content (50 meq./100g fabric), which can be ascribed to its nature and its manufacturing conditions. This value increases remarkably as the amount of 3-bromopropionic acid is increased during the modification. This data supports the progressive reaction between the hydroxyl groups of viscose and the bromine atom of the 3-bromopropionic acid.

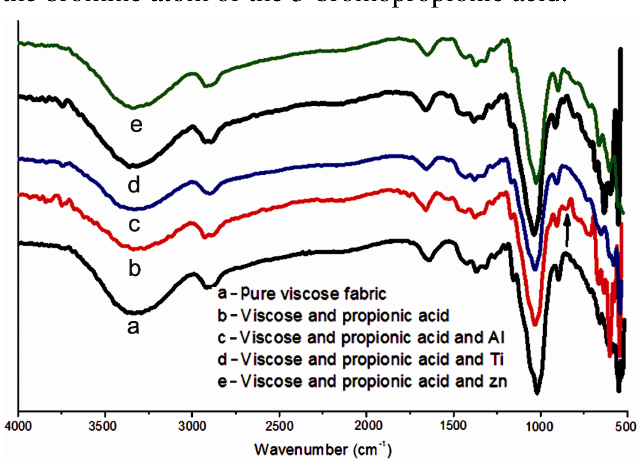

Fig. 1—FTIR spectra of untreated and pretreated viscose fabric with 3-bromopropionic acid and nano metals oxide

3.3 Effect of 3-Bromopropionic Acid Concentration on Nano Metal Oxides Uptake by Viscose Fabrics

The ability of carboxylic groups to attract and/or act as anchor on metal oxides, such as TiO_2 through electrostatic interaction, is an established fact[33,34]. The present study shows the ability of the carboxylic groups introduced to the viscose fabrics to attract the nano metal oxides such as aluminum oxide, zinc oxide or titanium (IV) oxide from their suspensions to the viscose fabrics. Figure 4 confirms the aforementioned fact that as the concentration of 3-bromopropionic acid is increased, the amount of nano metal up-take by the viscose fabric is also increased.

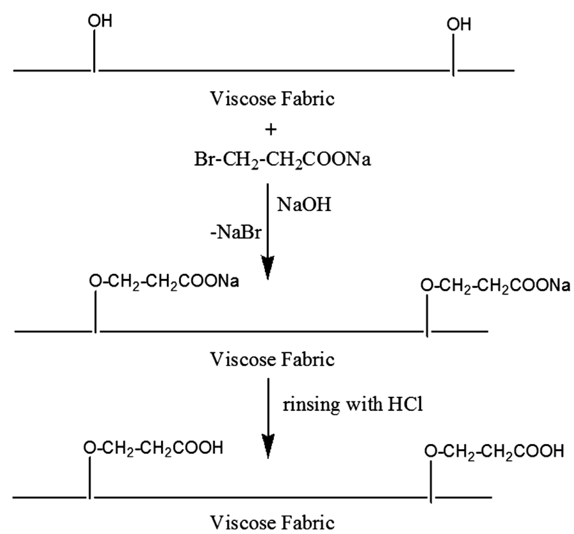

Fig. 2—Proposed reaction mechanism of 3-bromopropionic acid with viscose fabric

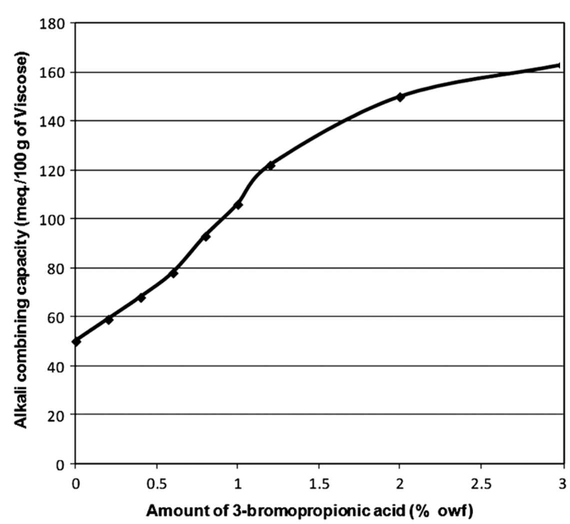

Fig. 3—Effect of concentration of 3-bromopropionic acid on alkali combining capacity of pretreated viscose fabric

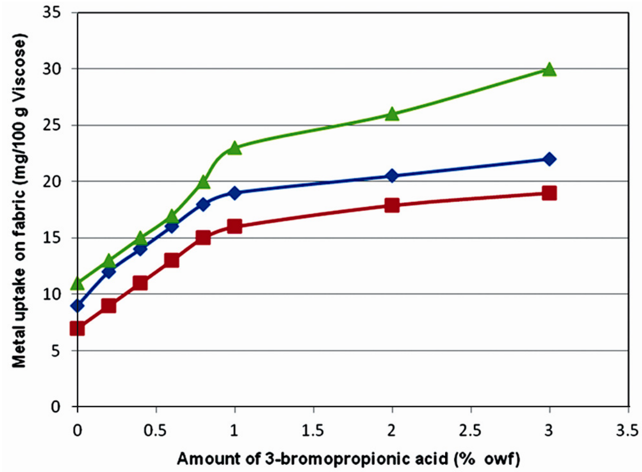

Fig. 4—Effect of concentration of 3-bromopropionic acid on nano metal oxides uptake by the viscose fabric

3.4 Antimicrobial Activity of Treated Viscose

Both untreated and 3-bromopropionic acid treated viscose fabrics, after treating with nano metal oxides (aluminum oxide, zinc oxide or titanium (IV) oxide), were subjected to a challenge for killing one of the most common Gram negative bacteria (*Escherichia coli*) as well as the famous fungus (*Candida albicans*).

Figures 5 (a) and (b) reveal the incapability of the 3- bromopropionic acid treated viscose fabrics to resist the microorganism's growth. On the contrary, a unique ability to stop growth of these microorganisms on the viscose fabric pretreated with 3-bromopropionic acid followed by treatment with nano metal oxides is also observed. It is also obvious that the ability of nano metal modified viscose fabrics to reduce the microbial growth is in the following order: zinc oxide > aluminum oxide > titanium (IV) oxide. The ability of nano metal oxide to decrease the number of viable microorganism colonies could be attributed to their environmental stress (reactive oxygen species level) on the bacterial cell wall, which may break down the cell wall and the outer membrane. This would allow cell contents to leak out and nano metal oxide to enter, thereby causing cell irregularities and depressions[35]. It is also obvious that 3-bromopropionic acid has a superior antifungal activity in comparison with its antibacterial activity.

3.5 Durability of Antimicrobial Activity of Treated Viscose Fabric

Viscose fabrics treated with nano metal oxides as well as viscose fabrics pretreated with 3-bromopropionic acid and/or nano metal oxides were exposed to 30 wash cycles to investigate their capability to resist the microbial growth. Table 1 shows that the viscose fabrics treated with 3-bromopropionic acid and after treated with nano metal oxides show superior reduction in the microorganism's growth, in comparison with those fabrics treated only with nano metal oxides.

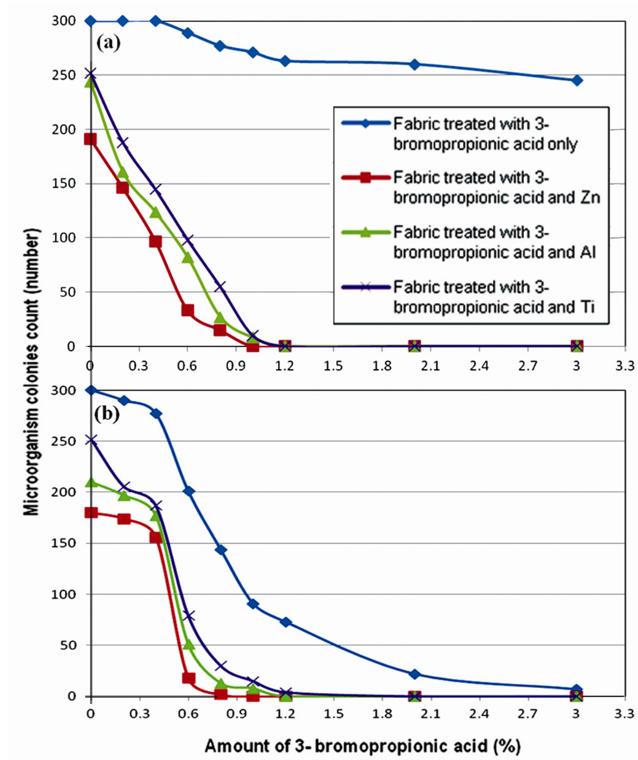

Fig. 5—Effect of 3-bromopropionic acid and nano metal oxides on antibacterial and antifungal activity of viscose fabric (a) antimicrobial activity and (b) antifungal activity

This verdict could be attributed to the higher concentration of nano metal oxides on the fabrics treated with 3-bromopropionic acid. The carboxylic groups added to the fabrics are not only acting as attracting groups for the nano metal oxides, but also fixing them on the fabric. This fact could be the reason behind the ability of the viscose fabrics, treated with 3-bromopropionic acid and nano metal oxides, to maintain their high antimicrobial activity even after 30 wash cycles.

3.6 TEM Study

The investigation of the morphology of the untreated as well as treated viscose fabrics demonstrates no clear difference in the morphological structure of the viscose fabrics after treatment with 3-bromopropionic acid and nano metal oxides Fig. 6. This could be attributed to the ability of the nano particles to form a transparent layer on the fabric surface.

Table 1—Effect of wash cycles on antibacterial and antifungal activities of untreated and treated viscose fabric

3-Bromopropionic acid concentration, %	Nano metal oxide	Reduction percentage after different wash cycles			
		5	10	20	30
Antibacterial activity					
0	-	N	N	N	N
1	-	8.0	7.5	7.5	6.5
0	ZnO	39.0	9.5	N	N
	Al_2O_3	21.5	N	N	N
	TiO_2	16.0	N	N	N
1	ZnO	100	100	100	97.0
	Al_2O_3	94.0	91.5	89	86.5
	TiO_2	91.0	90.0	87.0	83.5
Antifungal activity					
0	-	N	N	N	N
1	-	64.0	63.5	60.5	57.5
0	ZnO	37.0	N	N	N
	Al_2O_3	25.0	N	N	N
	TiO_2	14.0	N	N	N
1	ZnO	100	100	100	97.5
	Al_2O_3	97.0	96.0	95.0	93.5
	TiO_2	96.5	96.0	95.0	92.5

N = No microbiol reduction

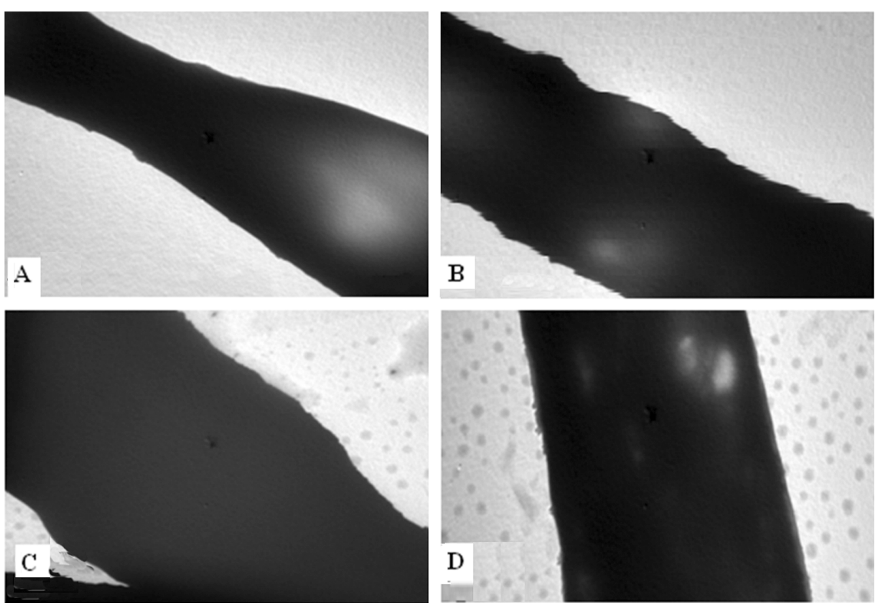

Fig. 6—TEM of untreated and pretreated viscose fabrics with 3-bromopropionic acid & nano metal oxides [A—Untreated viscose, B—pretreated viscose + Zn, C—pretreated viscose + Al and D—pretreated viscose + Ti].

4 Conclusion

FTIR spectra of untreated viscose fabric as well as fabrics pretreated with 3-bromopropionic acid and then with nano metals shows a support for the reaction between the viscose fabrics and 3-bromopropionic acid. The alkali combining capacity values increase remarkably as the amount of 3-bromopropionic acid is increased during the modification of the viscose fabrics, which supports the reaction between –OH active group of viscose and Br halide of 3-bromopropionic acid. The present study shows the ability of the introduced carboxylic groups to attract the nano metal oxides from their suspension to the fabrics. The study also shows the incapability of the 3-bromopropionic acid treated viscose fabrics to resist microorganism's growth. A unique ability to stop growth of these microorganisms on the viscose fabric can only be attained when treated with 3-bromopropionic acid followed by after treatment with nano metal oxides. It is also obvious that the ability of nano metal treated viscose fabrics to reduce the microbial growth is in the following order: zinc oxide > aluminum oxide > titanium (IV) oxide. 3-Bromopropionic acid has a superior antifungal activity in comparison with its antibacterial activity. The added carboxylic groups to the fabrics is not only acting as attracting groups for the nano metal oxides, but also fixing these nano metal oxides to the fabric. The viscose fabrics treated with 3-bromopropionic acid and nano metal oxides are found able to maintain high antimicrobial activity even after 30 wash cycles.

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