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Construction of durable antibacterial and anti-mildew cotton fabric based on P(DMDAAC-AGE)/Ag/ZnO composites

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ABSTRACT

To prepare antibacterial cotton fabrics with laundering durability, an organic-inorganic P(DMDAAC-AGE)/Ag/ZnO composite was synthesized by free radical polymerization where the epoxy groups were utilized to form covalent bonds with the hydroxyl groups of cotton fabrics. The surface morphology, crystal phase and chemical structure of the obtained P(DMDAAC-AGE)/Ag/ZnO composite were characterized by XRD, FT-IR and TEM measurements. The resulting P(DMDAAC-AGE)/Ag/ZnO composite-functionalized cotton fabrics exhibited outstanding antibacterial activity and excellent laundering durability. In the antibacterial tests, the bacteriostatic reduction rate was greater than 99.75%, and remained over 99.00% even after 11 washing cycles (equivalent to 55 commercial or domestic laundering cycles). The antibacterial mechanism was also investigated, partly including release of ions and photocatalysis. Moreover, the coated cotton fabric possessed excellent anti-mildew performance and also maintained the basic properties of cotton fabric. These results suggest that the modified cotton fabrics may find potential applications in a wide variety of areas such as sportswears, socks, and medical textiles.

1. Introduction

In our daily life, it is inevitable to come into contact with a variety of bacteria, fungi and other microorganisms, which may rapidly grow and breed under suitable environmental conditions, and even spread diseases through contact and do harm to people's health (Tian, Zhai, Xu, & Liang, 2017). Various textiles provide a good living environment for these microorganisms because of massive cellulose and pores (Nischala, Rao, & Hebalkar, 2011). Finishing textile with antibacterial activity can not only inhibit the growth and reproduction of bacteria but also protect the textile from degradation by molds (Moritz & Geszke-Moritz, 2013). Therefore, increasing attention has been paid to the development of antibacterial fibers and textiles (Yu, Wang, & Lv, 2016). An ideal antibacterial finishing agent (AFA) can not only kill harmful microorganisms, prevent the spread of the disease, but also meet the basic requirements of the following three aspects: (a) the AFA products should not have too strong toxicity to the human body and the environment, or cause skin allergies and discomfort; (b) the performance or appearance of the textile can not be adversely affected, and should be compatible with the conventional finishing process; and (c) the AFA products should be durable enough to withstand repeated water washing (Simoncic & Tomsic, 2010).

Among the antibacterial agents, nano structures of TiO_2 (Chen et al., 2014), Ag (Budama, Çakır, Topel, & Hoda, 2013), and ZnO (Wang et al., 2014) have been intensively studied due to their remarkable photochemical/photophysical and antibacterial properties. Of these, nano ZnO is generally nontoxic, capable of photocatalytic oxidation, and chemically stable under exposure to high temperature. Furthermore, ZnO nanoparticles possess unique advantages, as compared to nano-Ag, such as lower costs, white color, and UV-blocking (Huang et al., 2008; Nair et al., 2009).

Several studies have shown that ZnO nanoparticles might be coated onto textile substrates (Hatamie et al., 2015). Petkova and co-authors reported a simultaneous sonochemical/enzymatic process for antibacterial coating of cotton with ZnO nanoparticles forming a multilayer coating of uniformly dispersed nanoparticles. The enzymatic treatment provides enhanced adhesion of the ZnO nanoparticles and the coated cotton inhibited the growth of the medically relevant *Staphylococcus aureus* and *Escherichia coli* by 67% and 100%, respectively (Petkova, Francesko, Perelshtein, Gedanken, & Tzanov, 2016). Prasad coated

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cotton fabric with ZnO nanoparticles via an in-situ synthesis method, imparting the textile with excellent antibacterial activity (> 98% against two pathogens, *Staphylococcus aureus* and *Klebsiella pneumoniae*) (Prasad, Arputharaj, Bharimalla, Patil, & Vigneshwaran, 2016). However, the applications of nano ZnO are limited due to rapid electron-hole recombination rate and its absorption limited to the UV range (Manna, Goswami, Shilpa, Sahu, & Rana, 2015). These issues can be mitigated by the deposition of noble metals (Aladpoosh & Montazer, 2016; Wang et al., 2015) coupling with carbon materials (Liu et al., 2018) and doping with metals or nonmetals (Manikandan et al., 2017; Rojas-Andrade et al., 2017). In our earlier research, we prepared Ce-doped ZnO (Ce-ZnO) by a co-precipitation method, and the antibacterial activity of Ce-ZnO coated cotton fabric showed a significant improvement, as compared with pure ZnO alone (Gao et al., 2017), whereas the durability and anti-mildew property need to be further improved.

Within the context of environmental protection, fabrics with long-term antibacterial activity that resists home laundering are urgently needed. The production of durable antibacterial textiles embedded with inorganic nanoparticles often requires time-consuming fabric pretreatments such as chemical or plasma activation, in addition to subsequent coating stabilization using different cross-linking techniques (Chen et al., 2011). These procedures often make the finishing steps tedious and/or increase the costs of production.

Polymer-based inorganic nanocomposite materials combine the unique mechanical, optical, biological and electrical properties of inorganic, organic and nanomaterials, and have been attracting a great deal of interest from diverse areas of research. Polymer chains may contain reactive groups, and combination with inorganic antibacterial agents has outstanding advantages. In particular, they may exhibit synergistic antibacterial effects, and improve adhesion to the substrates (Bao, Feng, Wang, Ma, & Tian, 2017; Liu et al., 2014; Schwartz et al., 2012). For instance, Jing et al synthesized poly[5,5-dimethyl-3-(3′-triethoxysilylpropyl)hydantoin] (PSPH) and coated it onto cotton fibers together with TiO_2 nanoparticles by chemical binding in one-bath process. N-halamine siloxanes (PSPH) containing three ethyoxy groups are likely to react with nano-TiO_2 and can be coated onto cotton to produce durable antibacterial fibers with improved UV stability. The strong antibacterial activity arises from the synergistic effect between TiO_2 nanoparticles and PSPH (Li et al., 2014).

In our previous research, we designed long-acting antibacterial nanocomposite through a simple in situ polymerization method. The epoxy group of P(AGE-DMDAAC)/ZnO composite interacted with the hydroxyl group on cotton fibers to enhance the fixation of the composite antimicrobial agent onto cotton fiber as well as its durability (Gao, Chen, Ma, Duan, & Zhang, 2014); however, this material showed no resistance against mold, which was needed in the textile industry. In this work, P(DMDAAC-AGE)/Ag/ZnO composite with reactive epoxy groups was synthesized from vinyl monomers containing diallyl dimethyl ammonium chloride (DMDAAC), allyl glycidyl ether (AGE) and modified Ag/ZnO nanoparticles, and used as a novel antibacterial agent that was covalently bound to the cotton surface through the bonding interactions between the epoxy groups in the polymer chains and hydroxyl groups on cotton fiber surfaces, as illustrated in Scheme 1. In addition, the antimicrobial and anti-mildew properties of such covalently functionalized textiles were analyzed. The chemical structure and surface topography of the fabricated cotton fabric were measured by energy dispersive X-Ray spectroscopy (EDX) and scanning electron microscopy (SEM). TEM analysis was also carried out to examine the kinetic process of P(DMDAAC-AGE)/Ag/ZnO in bactericidal activity.

2. Experimental section

2.1. Materials

Zinc acetate dehydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$, AR, Tianjin Kermel Chemical Reagents Co. Ltd., China), silver nitrate ($AgNO_3$, AR, Tianjin Hongyan Reagent Plant, China), sodium hydroxide (NaOH, AR, Tianjin Hongyan Reagent Plant, China), ethanol (AR, Tianjin Hongyan Reagent Plant, China), DMDAAC (60%, Shandong Luyue Chemical Industry Co. Ltd., China), AGE (AR, Hangzhou Silong Material Technology Co. Ltd., China), potassium per sulfate (KPS, AR, Tianjin Hengxing Chemical Reagents Manufacturing Co. Ltd., China), KH-570 (CP, Xi'an Chemical Reagents Co. Ltd., China), and hydrochloric acid (HCl, CP, Xi'an Chemical Reagents Co. Ltd., China) were all used without further purification. Bacteria *Escherichia coli* (*E. coli*), *Staphylococcus aureus* (*S. aureus*), and *Aspergillus flavus*(*A. flavus*) were kindly provided by Xi'an Microorganism Research Institution and incubated at 37 °C on a nutrient agar plate for 24 h before use. All the water used in process was distilled water.

2.2. Preparation of Ag/ZnO nanocomposite

Ag/ZnO nanocomposite was prepared through a simple wet chemical method. Zinc acetate dihydrate (6.4 g) and silver nitrate were dissolved into 30 mL distilled water (Ag/Zn mole ratio 0.3:20) respectively. Sodium hydroxide (11.2 g) was dissolved into 50 mL distilled water to form a solution. At 60 °C, the $Zn(AC)_2$ solution and NaOH solution were mixed under vigorous stirring for 3 h, into which was then added the silver nitrate solution which was subject to magnetic stirring for 2 h. The solution was heated at 90 °C for 3 h. The sample was collected by centrifugation, washed by distilled water and ethanol two times, and then dried, affording a yellow brown powder. The pure ZnO nanoparticles were also prepared using this method in the absence of silver nitrate.

2.3. Preparation of P(DMDAAC-AGE)/Ag/ZnO composite

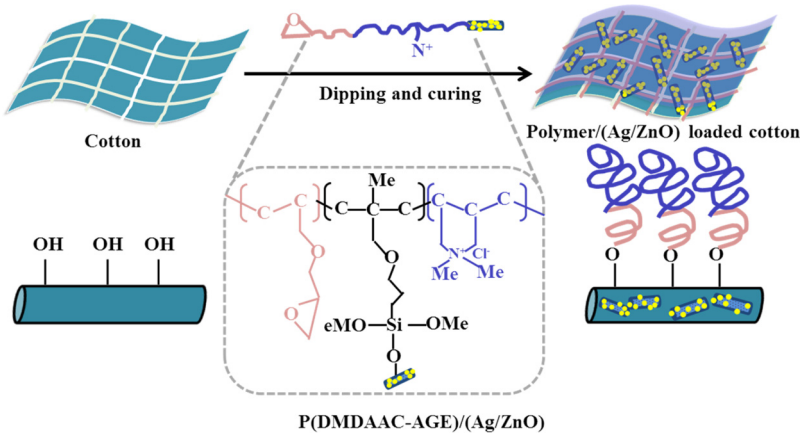
Silane coupling agent KH-570 (0.12 g) was added to a water suspension (30 mL) of Ag/ZnO (3.0 g) placed in a 250 mL three-necked round-bottom flask with a digital agitator and a reflux condenser under continuous stirring at 350 rpm, followed by DMDAAC (94 g) and KPS (13.3 g), and the reaction was run at 80 °C. Allyl glycidyl ether (1.5 g) and KPS (3.4 g) were then added after 20 min's stirring, then the same amounts of allyl glycidyl ether and KPS were added after another 20 min. The reaction was allowed to proceed for 3.5 h before the solution was cooled to room temperature, the pH was adjusted to 3.5 by using HCl, and the sample, P(DMDAAC-AGE)/Ag/ZnO composite, was obtained by centrifugation. For comparative purposes, P(DMDAAC-AGE)/ZnO was also prepared under identical conditions.

2.4. Application to cotton fabric

Cotton knitted fabrics (35 cm × 35 cm) were treated with P (DMDAAC-AGE)/Ag/ZnO nanocomposite. The samples were immersed in a P(DMDAAC-AGE)/Ag/ZnO solution (10–30 g/L) for padding and dried at 90 °C for 5 min in a preheated oven to remove the moisture, and then cured at 120 °C for 15 min. The Ag/ZnO and P(DMDAAC-AGE)/ZnO was also applied onto the fabric in the same manner as control groups.

2.5. Antibacterial property

The antibacterial activity of the treated fabric was tested against *Staphylococcus aureus* (*S. aureus*, ATCC6538), a Gram-positive bacterium, and *Escherichia coli* (*E. coli*, ATCC25922), a Gram-negative bacterium, by following the FZ/T 73023-2006 standard method (Chen et al., 2016). Finally, the bacterial were cultivated under light conditions and the specific illumination conditions were 8 W fluorescent lamp. The percent reduction of bacteria (i.e., the antibacterial rate, R) was calculated according to the following equation:



Scheme 1. Reaction mechanism between P(DMDAAC-AGE)/Ag/ZnO and cotton fabric.

$$R = (n_o - n_t)/n_o \quad (1)$$

where n_t is the number of bacteria recovered from the inoculated treated test specimen swatches in the jar incubated over the desired contact period (t), n_o is the number of bacteria recovered from the inoculated treated test specimen swatches in the jar immediately after inoculation (t = 0). The number of bacteria is counted by the colony counter.

The durability of antibacterial property was anlyzed by the AATCC test method 61-2007: "Colorfastness to Laundering: Accelerated" (Yang, Xu, & Zhang, 2017). A treated fabric samples were washed with ten steel balls (diameter 6 mm) in 200 mL of 0.37% soap at 40 °C for 45 min. Then the samples were dried in ambient. The treated cotton samples were washed for different time cycles (1 time cycle washing was equivalent to 5 times house laundering cycle).

2.6. Anti-mildew property

The anti-mold activity of the treated and untreated control cotton fabrics were tested against *Aspergillus flavus* (ATCC 204304) and the qualitative evaluation was carried out according to the standard GB/T 24346-2009 (Textile-Evaluation for anti-mould activity) (Yu et al., 2015).

2.7. Characterization

The P(DMDAAC-AGE)/ZnO and P(DMDAAC-AGE)/Ag/ZnO composites synthesized above were washed with acetone and ethanol three times and then dried at 105 °C for 6 h. FTIR spectra were recorded with a Bruker VECTOR-22 IR spectrometer at the resolution of 2 cm^{-1}. X-ray diffraction (XRD) measurements were carried out on a X-ray diffractometer remoter (Rigaku, D/max-2200, Japan) using Cu Kα radiation. The morphology was analyzed on a Jeol H-7650 transmission electron microscope (TEM). Scanning electron microscopy (SEM) images were obtained on a Hitachi S-4800 field emission scanning electron microscope, which is equipped with energy disperse X-ray spectroscopy (EDX) for elemental analysis. The thermal stabilities of native and treated cotton were evaluated by TG on a STA449F3-1053-M thermogravimetric analyzer (NETZSCH, Germany) from 30 °C to 600 °C at a heating rate of 10 K/min under nitrogen.

3. Results and discussion

3.1. Structural characterization of P(DMDAAC-AGE)/Ag/ZnO composites

3.1.1. XRD patterns

The XRD patterns of ZnO, Ag/ZnO, P(DMDAAC-AGE)/ZnO and P(DMDAAC-AGE)/Ag/ZnO composites are shown in Fig. 1. The peaks at 31.8°, 34.4° and 36.2°can be assigned to the (100), (002) and (101) lattice plane of nano ZnO (Svetlichnyi, Shabalina, Lapin, Goncharova, & Nemoykina, 2016), which were in good agreement with the JCPDS no. 36-1451 (Fig. 1a). Compared with pure ZnO, the typical peaks of Ag/ZnO have a blue shift, which meant the size of ZnO have a slight increase that can be attributable to the nano Ag deposited on the surface of ZnO(Fig. 1b). (Agnihotri, Bajaj, Mukherji, & Mukherji, 2015; Lu et al., 2017; Nagaraju, Udayabhanu, Prashanth, Shastri, & Yathish, 2017). This result was agree well with the results in the TEM analyse. The diffraction patterns of P(DMDAAC-AGE)/ZnO composites showed peaks at 34.4° and 36.2°, which correspond to the diffractions of ZnO (002) and (101) planes (Fig. 1d). An additional peak at 38° in the P(DMDAAC-AGE)/Ag/ZnO composite may be due to nano sliver (Fig. 1e). These results indicated that the P(DMDAAC-AGE)/ZnO and P(DMDAAC-AGE)/Ag/ZnO composites were successfully prepared, and both Ag and ZnO crystal structures were retained in the P(DMDAAC-AGE)/Ag/ZnO composite. Notably, the diffraction peaks of P(DMDAAC-AGE)/ZnO and P(DMDAAC-AGE)/Ag/ZnO composites were less intense and broader than those of Ag/ZnO.

3.1.2. FTIR analysis

Fig. 2 shows the FTIR spectra of Ag/ZnO, P(DMDAAC-AGE)/ZnO and P(DMDAAC-AGE)/Ag/ZnO composites. For Ag/ZnO, two broad peaks can be observed at ~3510 cm^{-1} and 1635 cm^{-1} arising from the −OH groups on the Ag/ZnO surface. The intense peak at ~465 cm^{-1} may be assigned to the Zn-O vibrational band of zinc oxide (Mohamed, El-Sheikh, & Waly, 2014; Perelshtein et al., 2009). For the P(DMDAAC-AGE)/Ag/ZnO composite, the band at ~3400 cm^{-1} is due to the stretching vibrations of the −OH groups on the surface of ZnO nanoparticles. The bands at ~2930 cm^{-1} and ~1231 cm^{-1} are attributed to the vibration of the $-CH_3$ and $-CH_2$ groups from KH-570, which means that the Ag/ZnO was likely functionalized with the silane coupling agent (Hang et al., 2015). The N-$(CH_3)_2$ stretching vibrations from DMDAAC monomer appeared at 2822 cm^{-1} (Chen et al., 2017). The broad weak peak at ~945 cm^{-1} was due to the stretching vibration of C—O—C in the ring and the ether (Druvari et al., 2016). The peak at ~620 cm^{-1} was assigned to Si—O—Zn (Gao, Duan, Chen, Lv, & Ma, 2015). Notably, no peaks corresponding to C=C were observed in the P(DMDAAC-AGE)/Ag/ZnO spectrum. This indicated that P(DMDAAC-AGE)/Ag/ZnO composite was successfully fabricated by the free radical polymerization reaction between modified Ag/ZnO and vinyl monomers (Jo, Choi, Choi, & Kim, 2016).

3.1.3. Morphological analysis

The morphology of the composites was examined by TEM measurements and shown in Fig. 3. The ZnO nanoparticles showed a rod shape with ~170 nm in length and ~30 nm in diameter, and the

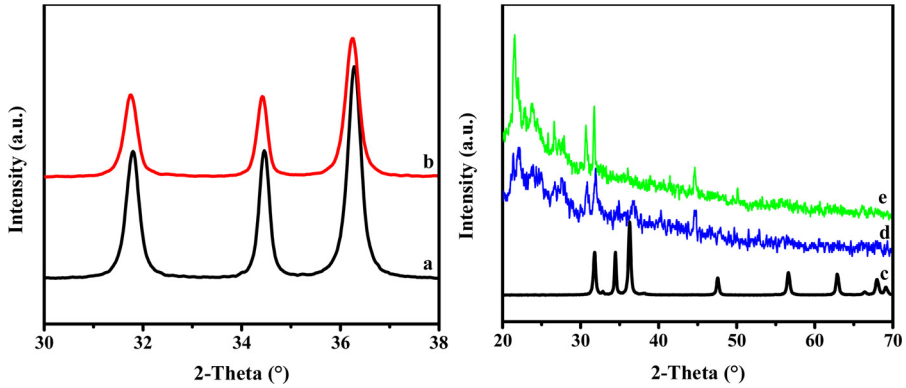


Fig. 1. XRD patterns of the as-prepared pure ZnO (a); Ag/ZnO (b), (2θ = 30～38°); Ag/ZnO (c), P(DMDAAC-AGE)/ZnO (d) and P(DMDAAC AGE)/Ag/ZnO composites (e), (2θ = 20～70°).

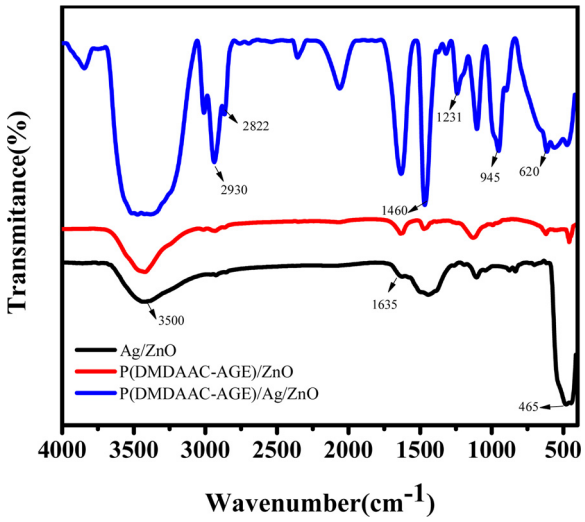


Fig. 2. FT-IR spectra of Ag/ZnO, P(DMDAAC-AGE)/ZnO and P(DMDAAC-AGE)/Ag/ZnO composite.

surface was smooth without other impurity particles (Fig. 3a). The morphology of Ag/ZnO was showed in Fig. 3b, where silver nanoparticles were deposited on the surface of nano-ZnO showing a spherical shaped and a diameter of about 15 nm.

Note that the uniform dispersion of nano fillers inside a polymer is important for the polymer composite to achieve a good filler-matrix interfacial adhesion. However, nanoparticles have strong tendency to form agglomerates due to its high specific surface area and the nano size effect. The morphology of the P(DMDAAC-AGE)/Ag/ZnO composite is showed in Fig. 3c. In comparison with Fig. 3b, nano sliver (marked with a red circle) and rod-like nano ZnO (marked with a yellow circle) are separated and dispersed in the matrix of the composite material. This may be due to the strong agitation in the polymerization process. The Ag/ZnO was modified with KH-570, and grafted with poly(quaternary ammonium salt-epoxy), which reduced the number of nanoparticle agglomerates and improved their compatibility with the matrix, thereby promoting their interfacial adhesion with the polymer matrix. Moreover, nano ZnO showed a needle-like shape, with varied diameter along the long axis, which may be due to the acidic pH in the solution that led to corrosion of the rod-shaped nano ZnO, changing the nano ZnO morphology and size.

3.2. Antibacterial property

The antibacterial activity of cotton fabrics coated with these composite materials was then determined using the Gram-positive *S. aureus*, Gram-negative *E. coli*. As shown in Table 1, the antibacterial rate of ZnO-coated cotton against *E. coli* and *S. aureus* were ～72% and 78%, respectively. After the modification with Ag, the inhibition rate on the two kinds of bacteria increased to ～78%, and ～88%. In addition, antimicrobial activity of the finished fabric against fungi *Candida albicans* (*C. albicans*) was also investigated. The antibacterial activity against *C. albicans* was improved from ～70% to ～97% after modified with Ag. Ag was considered as a scavenger to capture electrons, and then reduced the recombination rate of electron-hole pair to generate more reactive oxygen species, such as H_2O_2, O^{2-} and OH, which are toxic to the cells as they damage cellular constituents, then improved the photo-catalytic antibacterial activity of ZnO (Liu et al., 2014).

However, the result became unsatisfactory after 11 times of mechanical washing, likely because the bactericidal activity of either ZnO or Ag/ZnO coated cotton fabric had significantly decreased in the absence of a strong chemical bond. When ZnO nanoparticles were incorporated into the P(DMDAAC-AGE)-based composites, the antibacterial activity of P(DMDAAC-AGE)/ZnO coated cotton increased obviously; and even after 11 washing times, the antibacterial rate showed only a slight decrease, suggesting improved washing fastness between P(DMDAAC-AGE)/ZnO and cotton fabric. Actually among the series of samples, P(DMDAAC-AGE)/Ag/ZnO exhibited the highest

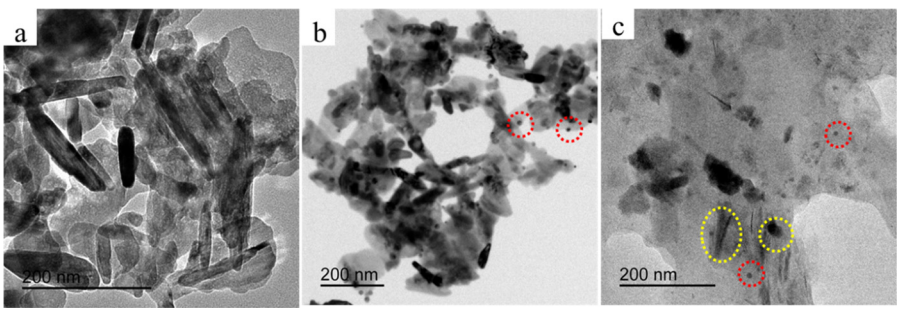


Fig. 3. TEM image of ZnO (a), Ag/ZnO (b) amd P(DMDAAC-AGE)/Ag/ZnO composites (c).

Table 1
Antibacterial rate of cotton fabric treated with ZnO, Ag/ZnO, P(DMDAAC-AGE)/ZnO and P(DMDAAC-AGE)/Ag/ZnO composite after different washing times (the concentration was 25 g/L).

Samples	Percentage Reduction against bacterial after different washing times (%)					
	E. coli (0 times)	*E. coli* (11 times)	*S. aureus* (0 times)	*S.aureus* (11 times)	*C. albicans* (0 times)	*C. albicans* (11 times)
ZnO	(72.1 ± 0.2)	(58 ± 0.4)	(78.3 ± 0.4)	(50.0 ± 0.2)	(69.9 ± 0.4)	(57.9 ± 0.2)
Ag/ZnO	(78.3 ± 0.3)	(62 ± 0.3)	(87.9 ± 0.7)	(58 ± 0.3)	(96.0 ± 0.7)	(79.1 ± 0.8)
P(DMDAAC-AGE)/ZnO	(88.8 ± 0.7)	(76 ± 0.7)	(87.1 ± 0.4)	(74.0 ± 0.4)	(88.9 ± 0.5)	(74.1 ± 0.9)
P(DMDAAC-AGE)/Ag/ZnO	(99.7 ± 0.1)	(99.3 ± 0.2)	(99.0 ± 0.1)	(98.6 ± 0.4)	(99.6 ± 0.3)	(93.8 ± 0.3)

antibacterial rate and retained almost 100% even after 11 laundering times, which can be attributed to the synergistic effect among Ag, ZnO and quaternary ammonium salt (Qi, Cheng, Yu, & Ho, 2017). Moreover, the covalent bond formed by the hydroxyl group of polymers and the epoxy group from the cotton fabric likely played an important role in the retention of this high antibacterial activity and stability.

3.3. Anti-mildew property

In addition to bacteria, mold also affects the appearance and comfort of textiles. Thus it is important to develop mildew-resistant textiles. Fig. 4 shows the anti-mildew property of cotton fabric before and after treatment with the various composite samples obtained above. We can clearly see that the native cotton fabric (Fig. 4a) and the ZnO-coated cotton (Fig. 4b) were both entirely covered with mold, indicating that these fabrics had no resistance for *A. flavus*. After ZnO was modified with Ag, a significant part of the cotton showed a clean surface without mold growth but the color appearance changed to yellow (Fig. 4c). When nano ZnO were introduced into the P(DMDAAC-AGE) based polymer, the coated cotton color remained white, but showed no resistance against *A. flavus* (Fig. 4d). By contrast, when Ag/ZnO nanoparticles were introduced into the P(DMDAAC-AGE) polymer, the modified cotton retained the original white color, showing excellent mildew resistance (Fig. 4e).

To investigate the durability of the anti-mildew performance of cotton fabric treated with P(DMDAAC-AGE)/Ag/ZnO), we cultured Petri dishes at controlled temperatures and humidity. Fig. 5 shows the mildew growth of P(DMDAAC-AGE)/Ag/ZnO) finished cotton fabric after different periods of time. The native cotton showed no resistance against mildew and was covered with mildew even in one day due to the abundant cellulose, while P(DMDAAC-AGE)/Ag/ZnO) coated cotton without washing displayed good anti-mildew property for three days, and became covered with numerous mildew after that. However, after 6 and 11 washing cycles, the anti-mildew property of the P (DMDAAC-AGE)/Ag/ZnO) coated cotton was markedly better than that of the unwashed cotton, and the anti-mildew property remained over 7 days. The anti-mildew level of the P(DMDAAC-AGE)/Ag/ZnO) coated cotton after 11 washing cycles even reached "0" (the best anti-mildew performance). Such remarkable anti-mildew property was likely due to silver ions produced by the composite. In the finishing process, the P (DMDAAC-AGE)/Ag/ZnO) formed a film on the cotton fiber, and silver ions were enwrapped in the film. During mechanical friction in the washing process, the film was destroyed, leading to a slow release of silver ions and thus an increasingly durable anti-mildew performance.

3.4. SEM and EDX analysis

The structures of the treated and untreated cotton fabrics were then examined by SEM and EDX studies, as illustrated in Fig. 6. In the SEM analysis, the native cotton fabrics showed a smooth surface without any impurities (Fig. 6a), while there were increasingly more wrinkled structures on the surface of the fibers after treatment with P(DMDAAC-AGE)/Ag/ZnO composites, which can be attributed to the aggregation of the grafted polymer chains (Wu et al., 2017). Moreover, some nanoparticles can also be observed in the sight that was due to the existence of Ag/ZnO particles (Fig. 6b). After 11 laundering cycles, much of the polymer remained on the cotton surface (Fig. 6c). It is worth noting that the composites were grafted on the cotton surface by the epoxy groups from the polymer chains.

Chemical composition of the cotton fabrics was then examined by EDX analysis. The results were reported based on both weight percentage (%W) and atomic percentage (%A) of the elements. As shown in the Fig. 6a1, the main elements of the native cotton fabrics included C and O. The content of Ag and ZnO can't be detected. After coating with P(DMDAAC-AGE)/Ag/ZnO composites, Ag and Zn elements from Ag/ZnO can be identified (Fig. 6b1). The *Wt*% of Ag and Zn element was 0.21% and 1.21% in the finished cotton fabric before washing. Interestingly, after washing 11 times, the content of Ag and Zn have a slight decrease with 0.17% and 0.94% weight percentage, respectively (insets to Fig. 6b1 and c1). The results shown that the P(DMDAAC-AGE)/Ag/ZnO composite can form stronger chemical bonds with cotton fabrics and retain effective antibacterial components after 11 repeated washing.

3.5. Antibacterial mechanism

To investigate the mechanism of the interactions between P (DMDAAC-AGE)/Ag/ZnO and bacterial cells, we chosen *S. aureus* as a model bacterium. TEM images in Fig. 7 clearly demonstrate close contact between P(DMDAAC-AGE)/Ag/ZnO and bacterial cells. Red arrows signified cell walls, and yellow circles represented the P (DMDAAC-AGE)/Ag/ZnO composite. The untreated *S. aureus* cells (Fig. 7a) can be seen to exhibit a spherical shape, smooth cell surface, and clear cell wall (Taglietti et al., 2012). However, remarkable

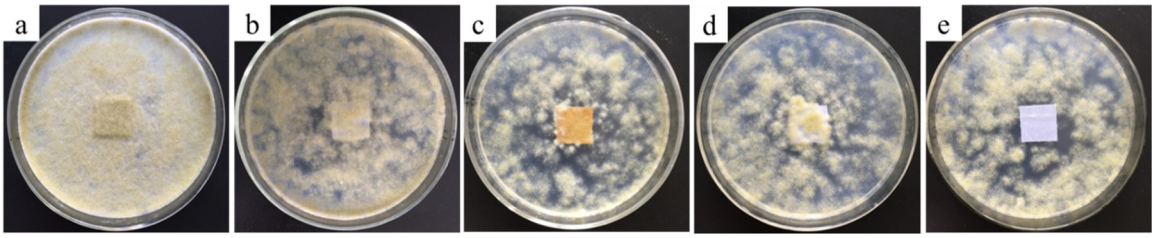


Fig. 4. Anti-mildew property of native cotton fabric (a); fabric treated with ZnO (b); Ag/ZnO (c); P(DMDAAC-AGE)/ZnO (d) and P(DMDAAC-AGE)/Ag/ZnO(e).

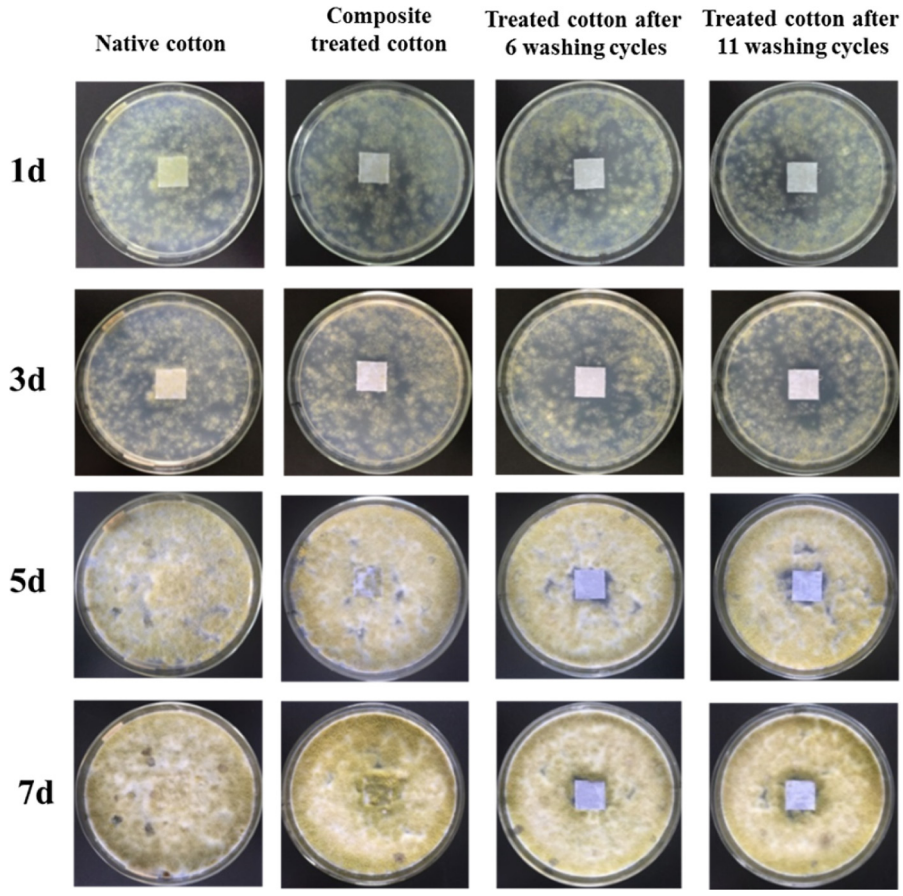


Fig. 5. Growth of *A. flavus* in different time periods after washing of cotton fabric with P (DMDAAC-AGE)/Ag/ZnO) composite materials.

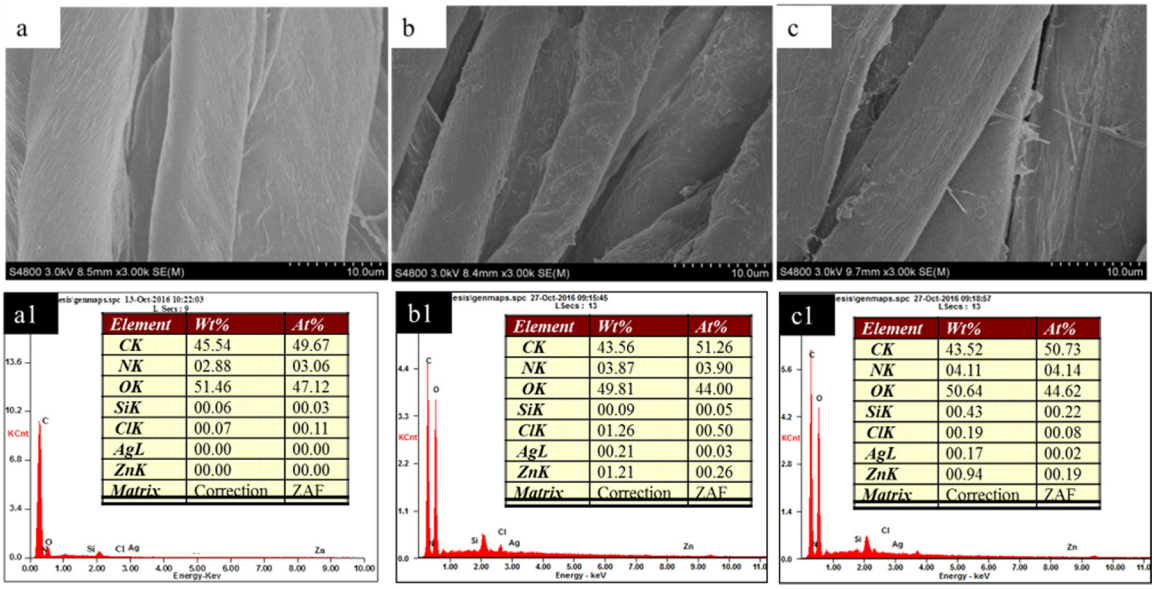


Fig. 6. SEM and EDX images of native cotton (a-a1); P(DMDAAC-AGE)/Ag/ZnO coated cotton (b-b1) and P(DMDAAC-AGE)/Ag/ZnO coated cotton after 11 washing times(c-c1).

changes in the cell walls can be observed after exposure to P(DMDAAC-AGE)/Ag/ZnO, where the composite (marked with yellow circles) was accumulated near the cell wall (Fig. 7b), suggesting that the composites likely adsorbed on the bacterial cytoderm and penetrated cytomembrane to impact the normal function of cells, which resulted in apoptosis (Lu et al., 2017). Moreover, one could see from the Fig. 7c that some of the cell walls were indeed destroyed or disintegrated. As the contact time increased between the composites and bacterial cells, an increasing number of cell walls were damaged, and the cytoplasm was leaking completely causing cell death (Fig. 7d–f) (Sun et al., 2017).

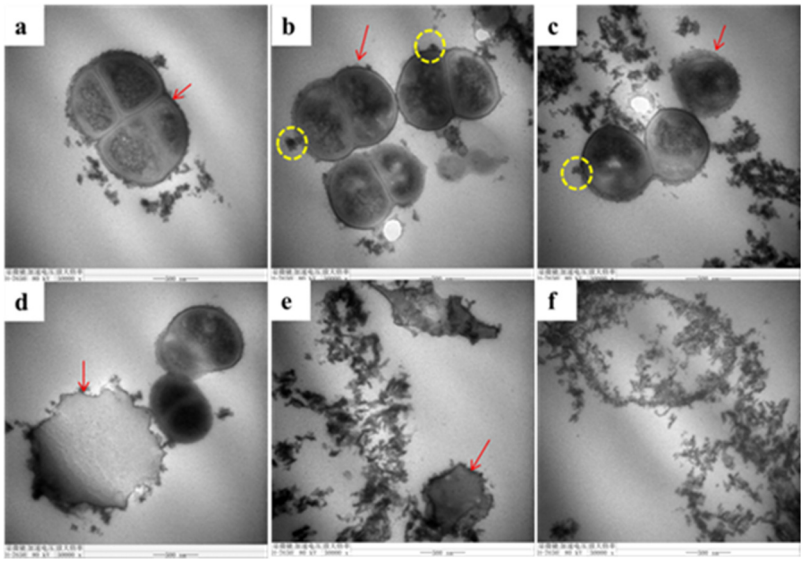


Fig. 7. The TEM images of S. aureus cells untreated (a) and after treated with P(DMDAAC-AGE)/Ag/ZnO (b-f).

3.6. Permeability and mechanical properties

To determine the influence of P(DMDAAC-AGE)/Ag/ZnO composite on the cotton fabric, the white index, softness, breaking elongation and air permeability were systematically investigated before and after treatment. The excellent softness of cotton textile is the main reason that catches so much people'love. After treated with obtained composite, the white index and softness of the cotton fabric can basically remain unchanged as we can see from Fig. 8a and Fig. 8b. The mechanical properties of cotton textiles are critical for the long-term stability. Fig. 8c shows the maximum breaking elongation increased from 62% to 73% in the weft direction. This was because the P(DMDAAC-AGE)/Ag/ZnO composite material formed a film on the surface of cotton fabrics with a certain flexibility (Lin et al., 2018), thus the maximum breaking elongation has been improved under external forces. Air permeability is an important evaluation criterion for the application of textile materials, which usually affect the wound recovery (Chen et al., 2014). In the commonly-used antibacterial finishing through a coating method, air permeability of the textiles would be severely reduced because the micropores of textile fibers are blocked by the coating layer (Zhang et al., 2018). The air permeability of native cotton was 23 (mL/(cm^2.s)). After treated with P(DMDAAC-AGE)/Ag/ZnO composite, the air

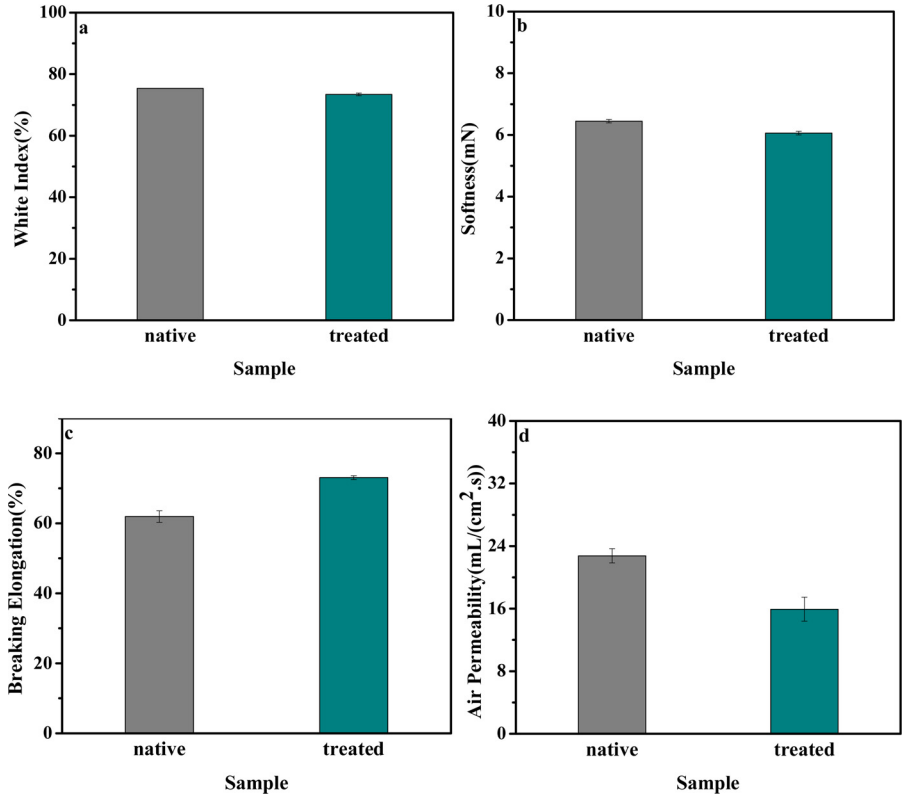


Fig. 8. Mechanical properties of cotton textiles before and after treated. (a) White index; (b) Softness; (c) Breaking elongation; (d) Air permeability. Errors bars were based on the standard deviations of three samples.

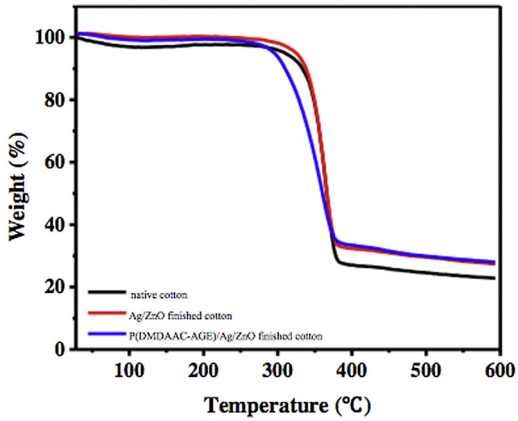


Fig. 9. TG curves of native cotton and cotton finished with Ag/ZnO and P (DMDAAC-AGE)/Ag/ZnO), respectively.

permeability of the textiles was reduced from ca. 23 to 16 (mL/(cm^2.s)). (Fig. 8d). Nevertheless, compared to some nanoparticles and polymer coatings, this reduction was mild and would not lead to an obvious influence on the textile applications.

3.7. Thermal analysis

In order to study the influence of our synthesised samples on the thermal properties of cotton fabrics, thermal analysis of native cotton fabrics and cotton fabrics finished with different samples in nitrogen atmosphere was carried out. The thermal stability curves of native cotton fabrics and cotton fabrics finished with different samples are shown in Fig. 9. The mass loss of cotton fabrics was about 5% when the temperature is lower than 200 C. This is mainly due to the volatilization of free water and bound water in cotton fibers. The main decomposition temperature of cellulose was 300–380 C (Lu, Jia, & Yang, 2018). The decomposition process of finished cotton fabrics is similar to that of native cotton fabrics. It can be seen from Fig. 9 that the decomposition temperature of native cotton fabric was 366.3℃, and that of residual carbon was only 22.82% when the temperature was 600℃. At the same time, the initial decomposition temperatures of cotton fabrics finished with Ag/ZnO nanoparticles and P(DMDAAC-AGE)/Ag/ZnO nanocomposite were 363.3℃ and 359.5 ℃respectively, and the carbon residue at 600℃ was 27.4% and 28.0% respectively. Obviously, due to the introduction of Ag/ZnO, the cotton fabric after finished had a high carbon residue. Moreover, the cotton fabric finished with P(DMDAAC-AGE)/Ag/ZnO nanocomposite had lower initial decomposition temperature than the native cotton and cotton fabric treated with Ag/ZnO. This can be explained by the organic segment of the polymer had a lower decomposition temperature than the Ag/ZnO and cellulose (Xu, Wei, & Dan, 2017).

4. Conclusion

A durable antimicrobial P(DMDAAC-AGE)/Ag/ZnO composite was synthesized by free radical polymerization. Cotton fabric functionalized with this composite exhibited outstanding antibacterial activities and also excellent laundering durability, inhibiting more than 99% of both *E. coli* and *S. aureus* even after 11 accelerated laundering cycles (equivalent to 55 commercial or domestic laundering cycles). Moreover, the modified cotton fabric displayed a remarkable anti-mildew property over seven days, and the anti-mildew level reached "0". Remarkable anti-mildew property was also observed even better after 11 washing cycles, as compared to the unwashed counterparts, likely due to the destruction of the polymer film that slowly released silver ions from the cotton substrate. This amazing performance and durability can be attributed to the P(DMDAAC-AGE)/Ag/ZnO composite where the epoxy group were covalently bonded to the hydroxyl group of the cotton fibers. It is not to be ignored that our work can endow the cotton fabric with functional properties while maintaining other physical and mechanical properties of native cotton fabric. Results from this study may be exploited for the preparation of cotton textile materials with strong antimicrobial and anti-mildew properties that can find use in practical applications, especially in biomedical textiles.

Notes

Authors declare no competing financial interest.

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