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# Preparation, characterization and antibacterial functionalization of cotton fabric using dimethyl diallyl ammonium chloride-allyl glycidyl ether-methacrylic/nano-ZnO composite

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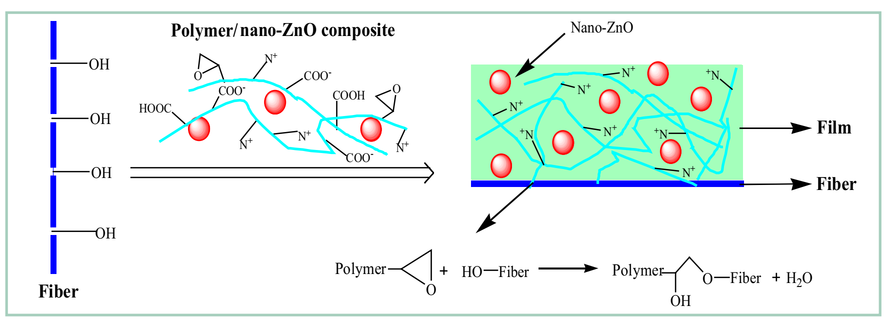
## HIGHLIGHTS

- The epoxy of composite could react with –OH of fiber to form chemical bonding.
- Nano-ZnO and $N^+$ could produce synergistic antimicrobial properties of fabric.
- The composites treated cottons had excellent antibacterial activities.

## GRAPHICAL ABSTRACT

The cotton fibers were treated with P(DMDAAC-AGE-MAA)/nano-ZnO composite in order to improve antibacterial properties via synergistic effect of nano-ZnO and $N^+$. The covalent bond between epoxy groups of composite and hydroxyl of the fiber can enhance the washing fastness of cotton fibers.

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## ABSTRACT

The polymer dimethyl diallyl ammonium chloride-allyl glycidyl ether-methacrylic shortened as P(DMDAAC-AGE-MAA) was prepared via free radical polymerization. P(DMDAAC-AGE-MAA)/nano-ZnO composites were obtained after mixing the polymer under different pH with nano-ZnO. P(DMDAAC-AGE-MAA)/nano-ZnO composites were characterized by Fourier transformation infrared (FT-IR), X-ray diffraction (XRD) and transmission electron microscopy (TEM). The results showed that nano-ZnO existed among the composites, and the polymer chain did not encapsulate nano-ZnO. The crystal structure of polymer changed because of the complexation of the polymer with nano-ZnO. The morphologies of P(DMDAAC-AGE-MAA)/nano-ZnO composites were core–shell and long strip structure when the pH of polymer was 2.6 and 3.0. After composite materials were loaded onto cotton fabrics, the surface morphology of the fabrics was characterized by scanning electron microscope (SEM). The antibacterial properties of P(DMDAAC-AGE-MAA) polymer and P(DMDAAC-AGE-MAA)/nano-ZnO composites treated cottons and treated cottons after being washed 5 times (equivalent of household washing 25 times) were tested against the bacterium *Staphylococcus aureus* (*S. aureus*, ATCC25923) and the fungus *Candida albicans* (*C. albicans*, ATCC10231). P(DMDAAC-AGE-MAA)/nano-ZnO treated cottons had higher antibacterial activities than P(DMDAAC-AGE-MAA) treated cottons.



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## 1. Introduction

Cotton fabric has excellent properties such as comfort, biodegradability and hygroscopicity on the human skin [1]. However, cotton fabrics also provide a suitable surrounding for the growth of microorganisms such as bacteria and fungi because of their hygroscopic properties, which result in their strong ability to absorb moisture. Antibacterial finishing agents are widely used to prevent microbes from breeding and harming people's health. So far, antibacterial agents can be broadly classified into two types: organic and inorganic.

Organic antibacterial materials possess high antibacterial efficiency, convenient process and stable color, etc. A large number of organic antibacterial agents such as quaternary ammonium [2,3], chitosan [4] and N-halamine [5,6] materials have been applied to impart antibacterial properties to the fabrics. In particular, quaternary ammonium antibacterial agents have been widely used to prevent the growth of microorganisms on the surface of fibers, but quaternary ammonium antibacterial agents will be ultimately exhausted, rendering the material ineffective. Dimethyl diallyl ammonium chloride (DMDAAC) is one of quaternary ammonium antibacterial agents, which can react with other monomers via radical polymerization because of the existence of double bond. Meanwhile, the functional monomers which can react with hydroxyl groups on the surface of cotton fiber were grafted onto DMDAAC used as a polymer backbone to circumvent the problem.

Inorganic antibacterial materials have a wide range antibacterial activity and high antibacterial efficiency, good heat resistance and safety, etc. Especially inorganic nano-particle antibacterial agents like zinc oxide (ZnO) [7–10], titanium dioxide [11,12] and silver nanoparticles [13,14] are popular in recent years. Among the nanoparticle antibacterial agents used, nano-ZnO belongs to a group of metal oxides having the following properties: antibacterial property, photocatalytic ability, electrical conductivity, photo-oxidizing capacity against chemical and biological species, and self-sterilization [15]. Nano-ZnO is generally regarded as a safe material for human beings and animals [16], and it has been used extensively in the formulation of personal care products, but compared with organic antibacterial agents, it often has lower binding force particularly at high pressure and high strength friction.

Organic–inorganic composite antibacterial agents are prepared by organic and inorganic nano-particle antibacterial materials, which can significantly improve the antibacterial efficiency and the combining fastness. In recent years, organic–inorganic composite antibacterials are preferred by researchers. Organic–inorganic composite antibacterials like chitosan/nano-ZnO [17], chitosan/AgCl–$TiO_2$ [18], polystyrene-block-poly (acrylic acid) copolymer/nano-ZnO [19], β-cyclodextrin/cotton/nano-ZnO [20] and chitosan/poly(ethylene glycol)/ZnO/Ag [21] composites have been applied to impart antibacterial properties to the fabrics. Inorganic nanoparticles are modified and dispersed by introducing organic components. In the polystyrene-block-poly (acrylic acid) copolymer/nano-ZnO composite, carboxyl functional group of organic components is a good modifier to improve the adhesion strength between inorganic nanoparticles and organic components [22]. Moreover, organic components are functional and crosslink with the fabric to enhance the extent of loading ZnO nanoparticles onto the fabrics.

The aim of this work is to improve the antibacterial activity of the cotton fabric by the synergy of the cation of $N^+$ and nano-ZnO. P(DMDAAC-AGE-MAA)/nano-ZnO composite was prepared by the polymer diallyl dimethyl ammonium chloride-allyl glycidyl ether-methacrylic P(DMDAAC-AGE-MAA) and nano-ZnO. The $COO^-$ of the polymer as a modifier could disperse nanoparticles, and the epoxy group of the polymer reacted with the –OH on cotton fibers to enhance the extent of fixation to the composite antibacterial agent onto cotton fiber as well as its durability. The antibacterial properties of the treated cotton fabrics, before and after washing, were investigated.

## 2. Experimental details

### 2.1. Materials

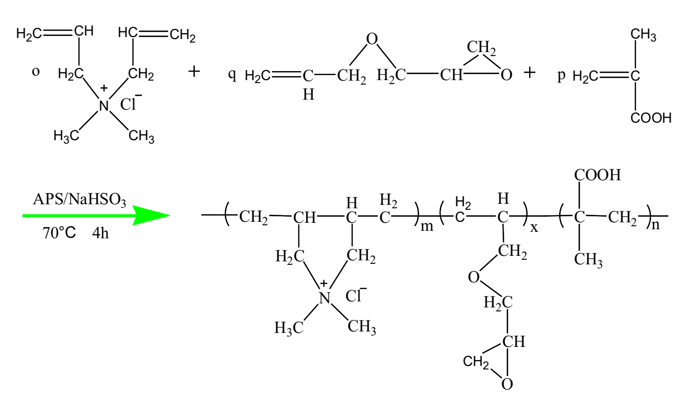
Dimethyl diallyl ammonium chloride (DMDAAC, 60%, Shandong Luyue Chemical Industry Co. Ltd., China), allyl glycidyl ether (AGE, AR, Hangzhou Silong Material Technology Co. Ltd., China), methacrylic acid (MAA, AR, Foshan Institute of Chemistry Pilot Plant, China), ammonium persulfate (APS, AR, Tianjin Hengxing Chemical Reagent Manufacturing Co. Ltd., China), sodium bisulfate ($NaHSO_3$, AR, Tianjin Tianli Chemical Reagent Co. Ltd., China) were all used without further purification. Nano-ZnO powder was purchased from Xiamen Jialu Metal Industries Ltd. and the diameter of nano-ZnO is 20 nm. The bacterium *Staphylococcus aureus* (*S. aureus*, ATCC25923) and the fungi *Candida albicans* (*C. albicans*, ATCC10231) were kindly provided by Xi'an Microorganism Research Institution and incubated at 37 °C on a nutrient agar plate for 24 h before use.

### 2.2. Synthesis of P(DMDAAC-AGE-MAA)

The synthetic route of P(DMDAAC-AGE-MAA) is presented in Scheme 1. Under continuous stirring at 350 rpm, dimethyl diallyl ammonium chloride (DMDAAC, 60%, 70 g) was poured into a 250 mL three-neck-flask equipped with a digital agitator and a reflux condenser in a water bath at 70 °C. Ingredient A allyl glycidyl ether (AGE, 1.0 g) was added into methacrylic acid (MAA, 2.8 g); ingredient B 0.0018 mol/ml APS solution with solid content of 4.2 g was added into 10 g of deionized water; ingredient C $NaHSO_3$ (0.47 g) was added to 10 g of deionized water. Then one of the three ingredients (A, B and C) was added into the flask. After being stirred for 15 min, one of the three ingredients (A, B and C) was added into the flask and another 20 g of deionized water. After being stirred for 15 min, the remaining ingredients (A, B and C) and another 20 g of deionized water were added into the flask. After 3.5 h, the solution was cooled to room temperature and the pH value was measured at 2.6.

### 2.3. Preparation of P(DMDAAC-AGE-MAA)/nano-ZnO composites

Under continuous stirring with 600 rpm, P(DMDAAC-AGE-MAA) solution (50 g) was poured into a 100 mL three-necked flask equipped with a digital agitator and a reflux condenser. The original pH value of the polymer was adjusted to 3.0 or 4.0 with 0.1 M




**Scheme 1.** The synthetic route of P(DMDAAC-AGE-MAA).