Durability of Nano ZnO Antibacterial Cotton Fabric to Sweat

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ABSTRACT: In this article, an innovative method was put forward to evaluate the endurance of nano ZnO finished fabrics to sweat. The atomic absorption spectrophotometer was used to determine the concentration of zinc in immersion liquor, and at the same time, SEM experiments and biocidal tests were chosen to characterize the antibacterial performance. Half-life time ($t_{1/2}$) of zinc concentration on the fabric was introduced to evaluate the durability to sweat. The results indicated that nano ZnO antibacterial cotton fabric was relatively sensitive to acid artificial sweat while durable in saline or alkaline solution, the $t_{1/2}$ exceeded 3000 min in them. SEM characterization and biocidal tests showed the same behavior. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 412–416, 2007

Key words: durability; antibacterial; atomic absorption spectrophotometer; half-life time

INTRODUCTION

The preparation of nano ZnO finishing agents and antibacterial cotton fabric has been reported previously[1,2]; however, the research on the durability of antibacterial cotton fabric has not been reported. The endurance of the antimicrobial functional fabrics mainly refers to the durability to washing, but in practice, clothes, especially the underclothes, frequently have contact with the skin and sweat closely.

The constituents of sweat mainly contain inorganic salts and organic compounds, the pH values of sweat show three types: acidic, alkaline, and neutral. In this work, artificial sweat was used to simulate the actual sweat.[3]

The content of Zn^{2+} can be tested by chemical or instrumental methods to determine the concentration of nano ZnO antibacterial agent on fabric. The instrumental methods were chosen because the zinc ion concentration was in milligram per liter magnitude in testing solution.[4] In this article, the migration of the nano ZnO on the fabrics in various artificial sweats were investigated with atomic absorption spectrophotometer (AAS), at the same time, antibacterial tests and SEM characterization as assistant methods were generally used to evaluate the endurance of antibacterial fabric.

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EXPERIMENTAL

Preparation of the artificial sweat

Acid artificial sweat solution was prepared with sodium chloride (8 g), carbamide (1 g), and lactic acid (2 g) dissolved in distilled water (1 L, pH ≈ 3). Alkaline artificial sweat solution was prepared with lysine (0.5 g), sodium chloride (5 g), and disodium hydrogen phosphate (2.5 g) dissolved in distilled water (1 L, pH = 8). Sodium bicarbonate (4.2 g), sodium chloride (0.5 g), and potassium carbonate (0.2 g) were dissolved in distilled water (1 L) to prepare inorganic salt artificial sweat solution, pH ≈ 8.

Preparation of nano ZnO antibacterial cotton fabrics

Half-bleached pure cotton fabrics (21 × 21) and the finishing agent (ZPU-1) in which the ZnO concentration is 11 g/L were selected in this work. Cotton fabrics were treated in a regular wet finishing process pad-dry method (wet pick-up rate, 100%) at room temperature. Two dips and nips were used. Treated fabrics were dried for 30 min at 100°C, and then stored in the desiccators. These treated samples were named ZNAC that would be used in the next research.

At room temperature, ZNAC samples were immersed in alkaline artificial sweat solution, acid artificial sweat solution, and inorganic salt artificial sweat solution respectively (liquid ratio 1 : 50). They were washed by stirring with constant velocity at 200 rpm for different times of 15, 30, 45, and 60 min.

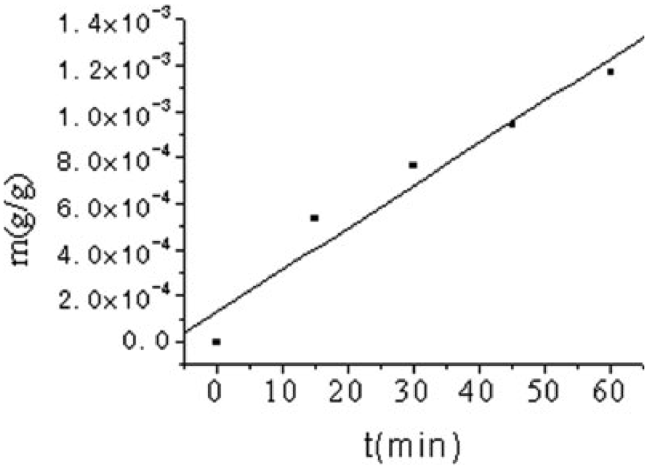

Figure 1 The zinc migration curve of ZNAC in acidic artificial sweat.

After washing, the solutions were diluted to 500 mL for AAS test. All of these operations were repeated five times and their average values were taken as the final results.

Zinc-migration property testing

The content of Zn in immersion liquid was examined by AAS (Shimadzu, AA-680). The hollow cathode lamp of Zn (the current was 7 mA), 213.8 nm wave length, air-acetylene flame, and 100 mm slit width were selected in this experiment.

Characterization of the fabrics treated with nano ZnO

The appearance, particle diameter, and distribution of nano ZnO on the immersed and unimmersed fabrics were characterized by SEM.

Test of antibacterial property

The antibacterial properties of treated fabrics with nano ZnO were tested according to the method of AATCC 90-1982.

RESULTS AND DISCUSSION

Migration character of nano ZnO on the fabrics in different media

To evaluate the migration character of ZnO in artificial sweats solution, for simplifying, an hypothetical linear relation between the migration amount of ZnO (m) and immersion time (t) was made. Thus, the curve of zinc migration could be expressed by eq. (1).

$$m = \mathrm{B}t + A \tag{1}$$

where B is the slope and A is the intercept.

The value of B or A implied the zinc migration, and the larger the value of B or A, the worse would be the endurance of nanoantibacterial fabric.

To use the curve of zinc migration to compare and analyze the endurance of nanoantibacterial fabric to sweat, we investigated the relationship between the zinc concentration (m) in immersion solution and the immersion time (t), especially defined zinc half-life time ($t_{1/2}$) on fabrics, thus, $t_{1/2}$ was inversely related to the zinc migration and was directly proportional to the durability.

The zinc migration curve of ZNAC in acidic artificial sweat solution was shown in Figure 1.

The migration equation was shown in eq. (2).

$$m = 1.838 \times 10^{-5}t + 1.293 \times 10^{-4} \tag{2}$$

where the relative coefficient (R) was 0.973.

The concentration of zinc on the fabric sample was determined to be 0.0168 g/g before immersion, at half-life time, m should be 0.0084 g/g, substituting 0.0084 g/g in eq. (2), then the value of $t_{1/2}$ = 449 min. The $t_{1/2}$ in different media was taken to evaluate the endurance of nano ZnO antibacterial fabric in different media.

The zinc migration curves of ZNAC in alkaline artificial sweat and inorganic salt artificial sweat were shown in Figures 2 and 3, respectively.

According to the same way, the obtained equations in alkaline artificial sweat and inorganic salt artificial sweat were $m = 2.28 \times 10^{-6}t - 8.88 \times 10^{-6}$ ($R = 0.990$) and $m = 2.09 \times 10^{-6}t + 3.10 \times 10^{-6}$ ($R = 0.999$), respectively; the $t_{1/2}$ of fabric in alkaline artificial sweat was 3656 min; in inorganic salt artificial sweat, $t_{1/2}$ was 3998 min.

To summarize all that mentioned earlier, we obtained the zinc half-life time in different immersion solution. The histograms of the zinc half-life times were shown in Figure 4.

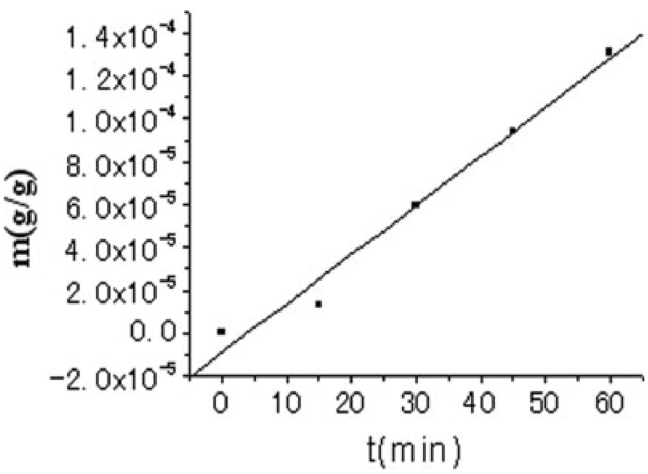

Figure 2 The zinc migration curve of ZNAC in alkaline artificial sweat.

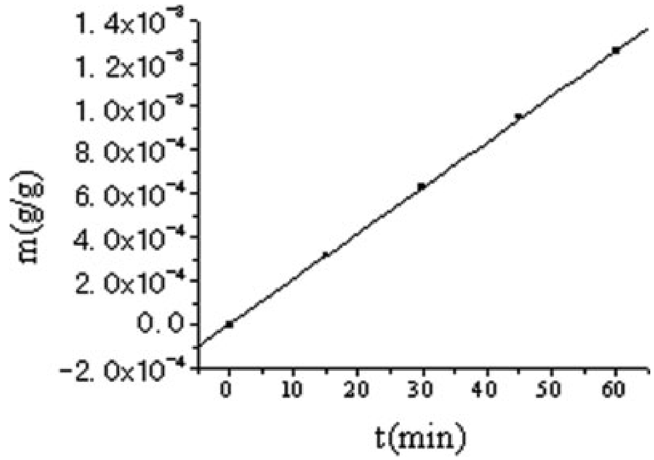

Figure 3 The zinc migration curve of ZNAC in inorganic salt artificial sweat.

From Figure 4, the zinc half-life time of the same sample in different sweats were different: $t_{1/2}$(salty sweat (pH $\approx$ 8)) $>$ $t_{1/2}$(alkaline sweat (pH $\approx$ 8)) $>$ $t_{1/2}$(acidic sweat (pH $\approx$ 3)).

The amphoteric compound, ZnO, was sensitive both to acid and alkali media, the reaction in acidic medium was as shown in eq. (3).

$$ZnO(s) + H^+(aq) \rightarrow Zn^{2+}(aq) + H_2O \quad (3)$$

The zinc half-life time ($t_{1/2}$) was the lowest in acidic artificial sweat (pH $\approx$ 3), and this proved the reaction eq. (3).

In alkaline medium, the reactions were as shown in eqs. (4) and (5).

$$ZnO(s) + OH^-(aq) \rightarrow Zn(OH)_2(s) + H_2O \quad (4)$$

$$Zn(OH)_2(s) + OH^-(aq) \rightarrow [Zn(OH)_4]^{2-}(aq) + H_2O \quad (5)$$

ZnO would be stable or react according to eq. (4) in alkalescent solution; as the pH value increased, $Zn(OH)_2$ would further react according to eq. (5), and the solubility of ZnO would be increased. But, in practice, the stability of ZNAC in alkalescent solution (pH $\approx$ 8) was very high, therefore the eq. (5) not occurred in the experimental condition.

ZnO could not only be affected in the acid–base condition, but also affected by the related compounds or ions like Zn^{2+}, $Zn(OH)_2$, and $[Zn(OH)_4]^{2-}$ called salt effects. The salt effect was one type of the common ion effects, and the zinc migration would be inhibited with the increase of cationic concentration in inorganic salt solution. The zinc migration in inorganic salt sweat was very small owing to the salty effect. Additionally, when the concentration of CO_3^{2-} in inorganic salt sweat was quite high, the following reaction [eq. (6)] occurred.

$$Zn^{2+}(aq) + CO_3^{2-}(aq) \rightarrow ZnCO_3(s) \quad (6)$$

Undissolved $ZnCO_3$ would deposit on the fabric, which induced the declination of the apparent solubility of ZnO. Since the human sweats were almost all alkalescence, their influences to the migration character of ZnO were usually weaker.

The research on antibacterial capability

Antibacterial properties of as-prepared fabrics, which were immersed for 200 min in ATCC 25922 *E. coli* and ATCC 25923 *S. aureus*, were examined according to Halo method. The results were shown in Table I.

Antibacterial ability (ψ) was positively proportional to the radius of antibacterial Halo (r), so we could believe the change of the Halo radius was equivalent to the change of the antibacterial ability. Table I showed that the antibacterial ability declined after immersing for 200 min, but the samples still had antibacterial effects and the entire Halo radius exceeded the national standard of 2 mm. Under illumination, all samples exhibited stronger antibacterial properties than under ordinary condition. Cotton fabrics also displayed stronger antibacterial properties to *S. aureus* than to *E. coli* because the *S. aureus* was gram-positive bacteria, while *E. coli* was gram-negative bacteria. It was known that the surface of ZnO nanoparticles carried negative charges. The order of antibacterial properties was in accordance with that of half-life times. On the other hand, this proved that the acid resistance was weaker, but salt and alkaline resistances were better.

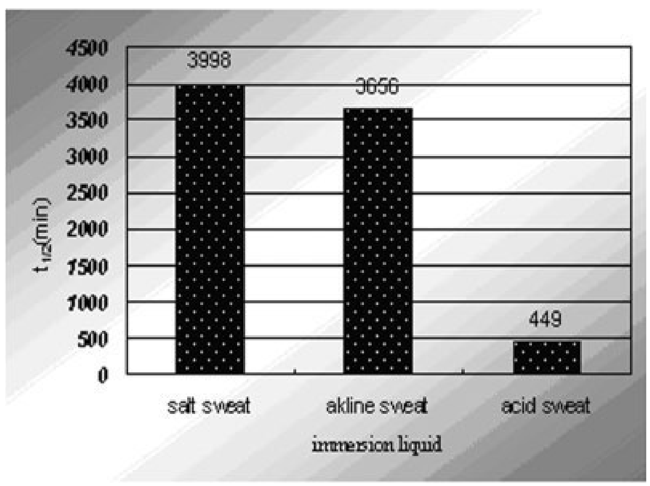

Figure 4 The histogram of the zinc half-attenuation time.

TABLE I
Radius of Antibacterial Halo of ZNAC after Immersing for 200 min

	Radius of antibacterial halo (mm)			
	E. coli		*S. aureus*	
Sweat	Nonillumination	Illumination	Nonillumination	Illumination
Acidity	3.3	3.5	3.6	4.1
Alkaline	4.5	4.9	4.9	5.5
Inorganic salt	4.7	5.2	5.1	5.8
Unimmersed	5.0	5.6	5.5	6.2

The change of ZNAC microtopography

In Figure 5, comparing Figure 5(a,b) with Figure 5(c,d), it could be seen that the distribution of ZnO nanoparticles on immersed ZNAC was similar to that on the unimmersed. Nano and subnanoparticles coexisted, although some particles, which mainly exist in the gaps of cotton fibers were partially congregated, and the distribution situations and consistencies of ZnO particles on the ZNAC surface were similar. All these demonstrated that the immersion process did not lead to ZnO migration largely. The existence of polymer film might prevent ZnO from migration.

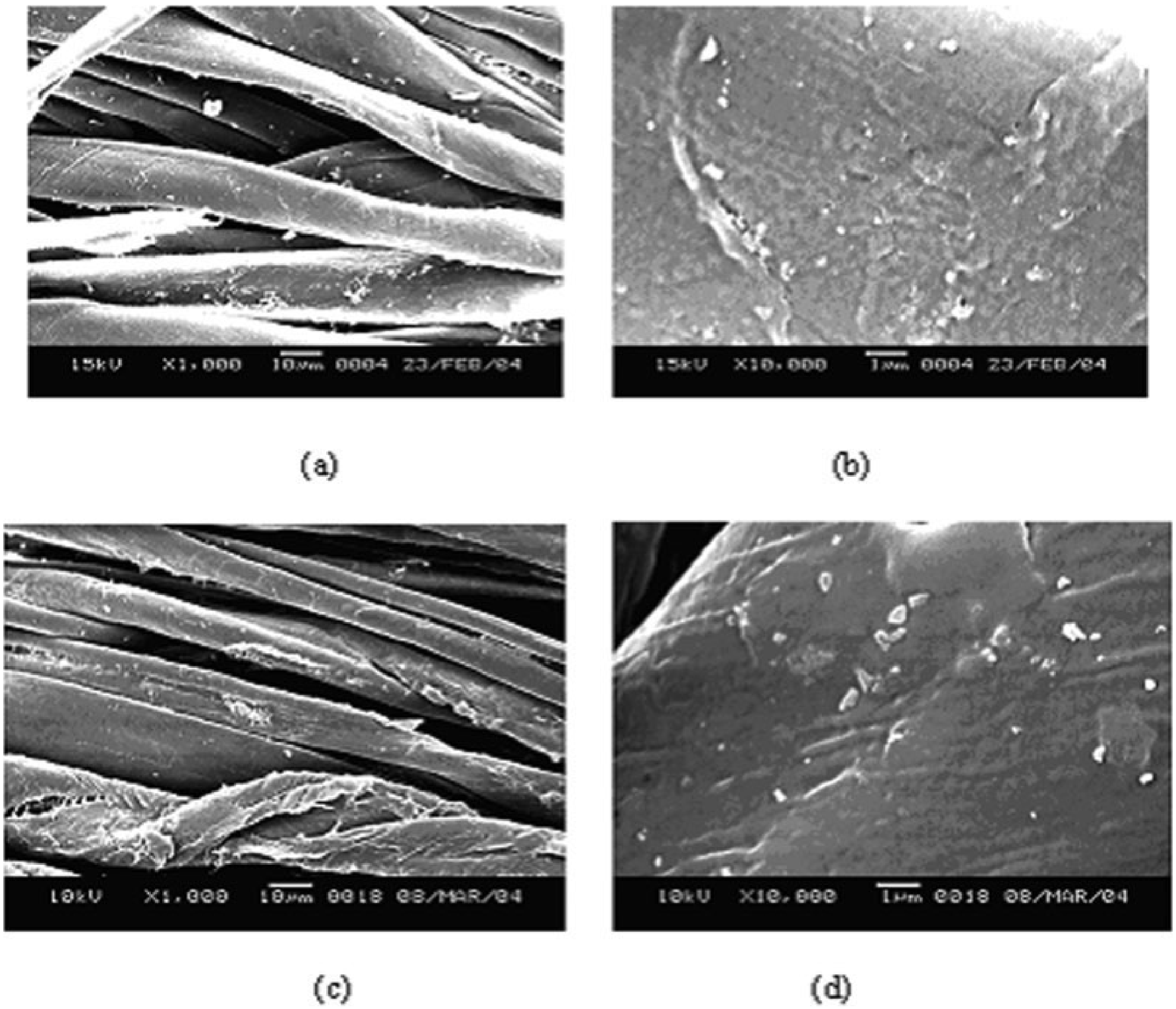

Figure 5 SEM images of the fabrics: (a) ZNAC sample, (b) partial of (a), (c) immersed ZNAC sample, and (d) partial of (c).

CONCLUSIONS

The fabrics treated with nano ZnO antibacterial finishing agent were immersed in artifical sweats. The zinc contents in the immersion solution were tested by AAS and the results showed that it was feasible to evaluate the durability of antibacterial function via the zinc half-life time ($t_{1/2}$) on cotton fabrics. The acid resistance of the nano ZnO antibacterial cotton fabrics was worse ($t_{1/2} < 450$ min), but their antibacterial performances were still good enough over national standard. The salt and alkali resistances were much better ($t_{1/2} > 3000$ min). SEM characterization and antibacterial tests showed the same situation as $t_{1/2}$ evaluations.

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