Microbial Detection, Surface Morphology, and Thermal Stability of Cotton and Cotton/Polyester Fabrics Treated with Antimicrobial Formulations by a Radiation Method

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ABSTRACT: Cotton and cotton/polyester fabrics were treated with a proposed antimicrobial formulation based on zinc oxide (ZnO), Impron MTP (binder), and Setamol WS (dispersing agent) under the effect of γ irradiation. The effect of this treatment on the growth of certain bacteria (*Bacillus subtilis*) and fungi (*Aspergillus niger*) was studied. In general, it has been confirmed that ZnO ratio is an inhibitory factor on the growth of both microbes. As a result of treatment of cotton fabrics, as an example, the *B. subtilis* counts were decreased by 4 log cycles whereas the *A. niger* count was decreased by 2 log cycles. This finding was illustrated by observing the surface microstructure of the fabrics after they had been buried in a moist soil for two weeks. The deterioration in the weaving structure of the nontreated was so strong that it could not distinguish the strings forming the fabric. On the basis of microbial detection, it was found that the treatment with ZnO formulation causes a net reduction in the bacterial cells amounts to 78 and 62% in the case of treated cotton and cotton/polyester fabrics while the net reduction in the fungi was calculated to be 80.7 and 32%, respectively. However, it was found that the treatment with ZnO formulation caused a reduction in the thermal stability of the fabrics as indicated by thermogravimetric analysis. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 2604–2610, 2003

Key words: radiation; fabrics; antimicrobes; morphology; thermal properties

INTRODUCTION

Microorganisms are spread everywhere; whenever there is some moisture and appropriate nutrient, they will thrive even under severe conditions. *Staphylococci, Salmonellas,* and *Pseudomanodes* are only a few germs that threaten human life by their destructive power. It has been reported that if we start with a single bacterium, after about 9 h, 6 billion bacteria will have developed.[1] Even though unpleasant odor and visual deterioration are indications of the growth of microbes, it is necessary to test the resistance of finishing agents applied to textiles toward certain microorganism by microbiological methods beside physical measurements. This is because these tests enable the researchers to develop the antimicrobial agents having specific inhibitory effect on certain microorganisms. In this regard, cotton fabrics treated with certain inorganic bactericides containing silver or silica–alumina give a fabric with extinction of 100% after exposure to a medium containing *Staphylococcus aureus*.[2] Also, cotton/polyester (50/50) fabric treated with a silver formulation exhibited a number of bacteria formation of 3.6×10^3 vs 6.0×10^4 for nontreated fabrics.[3] This treatment was done on a NaOCl-treated fabrics, but when this treatment was carried out on H_2O_2-treated fabric exhibits $\leq$10 mL vs 1.1×10^5 for a nontreated one.[4] Cotton fabric treated with a silver–ammine complex salt and TiO_2 gives fibers with bacteria extinction amounts of 100 and 98% after 30 washings.[5]

In the present work, an attempt was made to introduce a new antimicrobial formulation, based on different contents of ZnO, Impron MTP as a binder, and Setamol WS as a dispersing agent, for cotton and cotton/polyester fabrics. Thus, the effect of treatment with zinc oxide formulation on the growth of certain microorganisms representing bacteria and fungi was studied. In this regard, *Bacillus subtilis* and *Aspergillus niger* were chosen. The microbial studies involved the counting of the living microorganisms, inhibition, and observing the growth of microorganisms by scanning electron microscope (SEM). Moreover, the effect of this treatment on the thermal decomposition behavior was investigated by thermogravimetric analysis (TGA). The TGA thermograms were used to determine the kinetics of the thermal decomposition reaction.

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EXPERIMENTAL

Materials

Plain weave cotton and cotton/polyester blend fabrics were kindly supplied by Hossni Co., Cairo, Egypt. The cotton/polyester blend was made of cotton and polyester fibers at a ratio of 35 and 65%, respectively. Both fabrics were scoured, and bleached, and were not subjected to any finishing processes. It should be noted that hydrogen peroxide, sodium hydroxide, and a nonionic wetting agent were used in the scouring and bleaching processes at the factory. However, before use, they were washed with a solution containing 5g/L Na_2CO_3 and 2g/L detergent at 60°C to remove any undesired materials.

Reagents

A fine powder of zinc oxide of analytical grade was kindly supplied by Prolabo, France. Impron binder MTP, as a crosslinking agent and Setamol WS, as a dispersing agent, were obtained from Clariant (Switzerland) and BASF (Germany), respectively.

Treatment of textile fabrics with ZnO formulation

An aqueous solution containing the appropriate quantities of zinc oxide, binder, and dispersing agent was first prepared. The solution was continually stirred until zinc oxide is homogeneously dispersed. Cotton or cotton/polyester strips (30 × 6 cm) were impregnated in this dispersion for 5 min. The samples were then squeezed to a pick up of ~100%, air dried, and afterward subjected to fixation by radiation techniques. Irradiation to the required doses was carried out in the Co-60 γ cell at a dose rate of 0.276 kGy/h.

Bacterial and fungal viable counts[6]

Five milliliters from inoculated nutrient broth media were transferred to sterile test tubes for each strain of microorganisms. The test tubes were inoculated with the untreated and treated fabric samples whereas a noninoculated tubes taken as a control. After inoculation of the samples, the number of survivors of microorganisms for *B. subtilis* and *A. niger* were counted employing the one-tenth serial dilution technique and spreading 0.1 mL from each appropriate dilution in duplication on nutrient and Sabaroud agar plate, respectively. The average percent reduction in microorganisms were calculated as follows:

$$\text{Reduction (\%)} = [(N_C - N_S)/N_C] \times 100$$

whereN_C and N_S are the average numbers (cfu/mL) of viable microorganisms of the control and inoculated samples, respectively.

Scanning electron microscopy (SEM)

The surface morphology of cotton and cotton/polyester fabrics was examined by SEM. The SEM micrographs were taken with a JSM-5400 microscope made by Joel, Tokyo, Japan. A sputter coater was used to precoat conductive gold onto the surface before observing the microstructure at 30 kV.

Thermogravimetric analysis (TGA)

The thermal decomposition behavior of the nontreated and treated fabrics were investigated by thermogravemetric analysis (TGA) using a TG-50 instrument from Shimadzu (Tokyo, Japan) at a heating rate of 10°C/min. The data obtained from TGA curves were used to determine the rate of thermal decomposition, activation energy and order of reaction.

RESULTS AND DISCUSSION

Microbial detection

A large number of fungi, and a relatively small number of species of bacteria, are able to decompose cellulose. However, it has been now established that various families of bacteria were isolated from soil and environment in which textiles are subjected during use or storing. In the present work, the effect of ZnO formulation treatment of cotton and cotton/polyester fabrics on the survival of two types of microorganisms was investigated. In this regard, *B. subtilis* was chosen on the basis of being gram positive, which is more resistant than gram negative, while *A. niger* isolate, as a fungi, was introduced as an aflatoxin producer strain.

Table I shows the change in microbial counts and percentage reduction of living microorganisms on cotton and cotton/polyester fabrics before and after their treatment with different antimicrobial formulations under the effect of constant dose of 30 kGy of γ radiation. At this particular dose, ZnO formulations affords maximum efficiency as an antimicrobial agent in terms of the retention in tensile strength after burying in a soil rich with microorganisms for two weeks. Higher doses beyond this dose will cause degradation to cotton cellulose. It can be seen that the nontreated cotton/polyester fabric is more resistant than nontreated cotton fabric toward both types of microorganisms in terms of percentage reduction of living microorganisms after 48 h incubation. However, it seems that the nontreated cotton fabric is more resistant toward *B. subtilis* than *A. niger* on the same basis. On the other hand, the nontreated cotton/polyester fabric showed a higher resistance toward *A. niger* than *B. subtilis*.

As a result of the treatment of cotton fabric with the antimicrobial formulation containing 2% of ZnO, the

TABLE I
***Bacillus subtilis* and *Aspergillus niger*[a]Counts of Cotton and Cotton/Polyester Fabrics Before and After Treatment with Different ZnO Formulations Under the Effect of Constant Dose of γ Irradiation (30 kGy)[b] Irradiation**

Composition of formulation	Testing fabrics	Number of living microorganisms after 48 h (cfu/mL)	Microbial reduction (%)	Net reduction in microorganisms due to treatment (%)
2% ZnO + 2% binding agent	Control	3.2×10^9 (4.8×10^6)	—	—
	Nontreated cotton	2.5×10^9 (3.9×10^6)	21.88 (18.75)	—
	Nontreated cotton/polyester	2.0×10^9 (1.6×10^6)	37.50 (66.66)	—
	Treated cotton	8.5×10^3 (2.4×10^4)	99.97 (99.46)	78.10 (80.71)
	Treated cotton/polyester	6.2×10^5 (3.8×10^4)	99.98 (99.21)	62.48 (32.55)
0.5% ZnO + 2% binding agent	Control	8.0×10^6 (12.0×10^5)	—	—
	Treated cotton	3.0×10^6 (8.0×10^5)	62.50 (33.33)	40.62 (14.58)
	Treated cotton/polyester	3.0×10^6 (8.0×10^5)	90.00 (88.67)	52.50 (15.00)
2% ZnO + 1% binding agent	Control	6.0×10^7 (5.0×10^6)	—	—
	Treated cotton	2.4×10^6 (1.2×10^5)	96.00 (97.60)	74.12 (78.85)
	Treated cotton/polyester	1.8×10^4 (3.3×10^3)	99.97 (99.93)	62.47 (33.27)

[a] The data between brackets are for *Aspergillus niger* fungi
[b] The content of the dispersing agent is constant at 1% in all formulations.

B. subtilis counts decreased by 4 log cycles whereas the *A. niger* counts were decreased by 2 log cycles. However, the net reduction in *B. subtilis* and *A. niger* counts caused by this treatment were calculated to be 78.1 and 80.71%, respectively. These findings indicate that the *B. subtilis* is relatively more resistant toward this treatment than the *A. niger*. An opposite trend can be seen in the case of cotton/polyester fabrics, in which this treatment has a higher action on *B. subtilis* than *A. niger* in terms of the net percentage reduction.

As shown in Table I, when ZnO content in the antimicrobial formulation was decreased to 0.5%, the net percentage reduction in the survival microorganisms was greatly decreased. When the content of the binding agent was reduced from 2 to 1%, a slight decrease in the percentage net reduction in *B. subtilis* and *A. niger* was observed for cotton fabrics. However, nearly no effect in the percentage net reduction of both microbes was seen in the case of cotton/polyester blend as shown in Table I. The net reduction of microorganisms was greatly decreased in the case of treated cotton/polyester by reducing ZnO content from 2% to 0.5, particularly in the case of *A. niger.* It seems the change in the binding agent content has nearly no effect on the percentage net reduction of the living *B. subtilis* or *A. niger.*

On the basis of the above results, few points may be indicated: (1) The relative low resistance of nontreated cotton fabrics toward the bacteria or the fungi is due to the bleaching and nonionic wetting agents used in initial stages of fabric treatments. These materials have been reported to provide an active germicidal.[7,8] (2) The presence of the synthetic polyester component seems to afford some protection to cotton cellulose against the *B. subtilis* and not against *A. niger*.[9] (3) The additional protection to cotton or its blend with polyester provided by ZnO formulation against microorganisms can be explained on the basis that the treatment acts as a barrier or block preventing the microorganisms to attack the fabrics. (4) In terms of the net percentage reduction in the living microorganisms, the ZnO formulation showed an effective protection to cotton fabrics against fungi rather than bacteria. (5) Although the binder and the dispersing agents are important for fixing the formulation to fabrics, the ZnO compound is responsible for the microorganism inhibition.

Surface morphology by SEM

SEM was used to demonstrate that deterioration occurred in the microstructure of fabrics as a result of microorganism attack and also to clarify the effect of the treatment with ZnO formulation on the growth of microorganisms. Therefore, nontreated and treated cotton and cotton/polyester fabrics were buried in moist soil rich with microorganisms for two weeks. At the end of the buried period, the samples were gentlly washed with water to remove the adhered soil on the surface of fabrics and were examined by SEM as shown in Figures 1 and 2. It should be mentioned that all the fabrics were treated with a formulation containing 2% of ZnO, 2% of the binding Impron MTP, and 1% of the dispersing agent Setamol WS under the effect of a dose of 30 kGy of γ radiation. It is well known that soil offers ideal living conditions for different microorganisms including bacteria, fungi, and rot, which are strongly attack cellulosic materials and may contribute to progressive decomposition. As shown in Figure 1(A), the weaving structure of nontreated cotton fabric was completely damaged in such a way that it could not distinguish the strings of warp

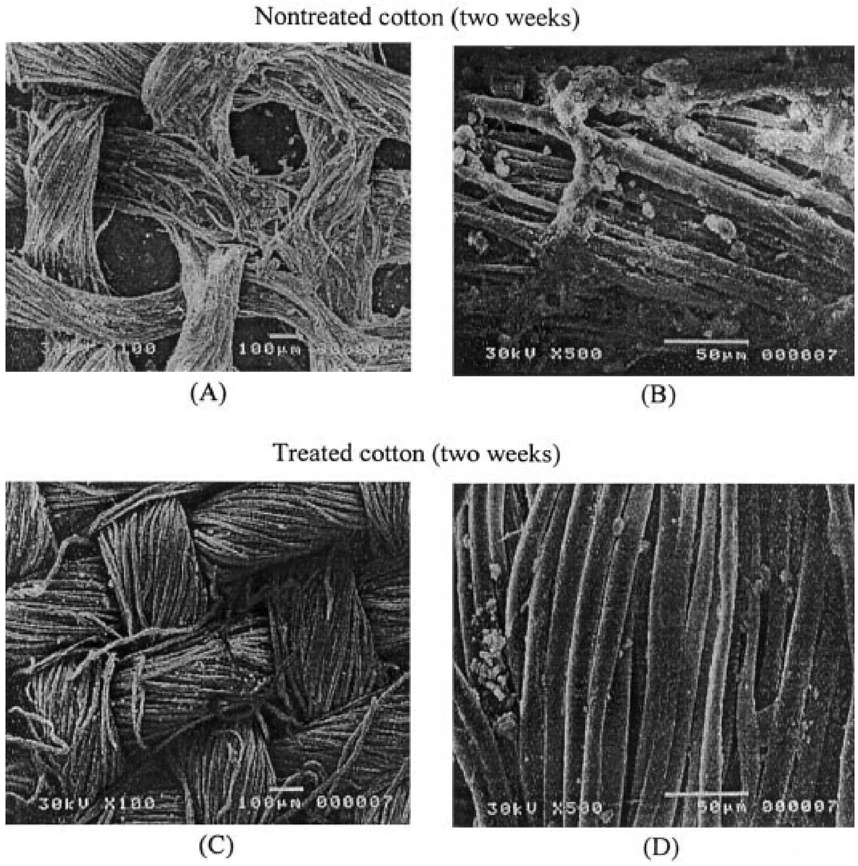

Figure 1 SEM micrographs of the surface morphology of nontreated cotton fabric (A and B) and treated cotton fabric with ZnO formulation under the effect of γ radiation at a dose of 30 kGy for antimicrobial finishing (C and D). All the fabrics were buried in an active moist soil for two weeks.

and weft directions. Also, there are great distances between the bundles of strings forming the fabric structure. The growth and dispersion of the microbes were clearly observed on the surface of fabrics in the form of spots, particularly in the magnified SEM micrograph shown in Figure 1(B). A different microstructure feature can be seen for the same fabrics treated with ZnO formulation as shown in Figure 1(C,D). The treatment prevents the attack of microorganism to the fabrics in which the weaving structure was not affected, and the strings forming the warp and weft directions can be distinguished. Also, a very small number of spots can be seen indicating the limited growth of microorganisms.

Unlike cotton, the nontreated cotton/polyester blend is more resistant to the growth of microorganisms, even though a deterioration can be seen as shown in Figure 2(A,B). However, the strings can be distinguished somewhat and the weaving structure still persist. However, the spots characterizing the microorganisms can be seen clearly. On the other hand, the treated cotton/polyester seems unaffected by the microorganisms in terms of the effect on weaving structure, microbial growth, and dispersion as shown in Figure 2(C, D).

Thermal stability

The thermal stability of any polymer material is largely determined by the strength of the covalent bond between the atoms forming the polymer molecules. The calculated dissociation energy for the different covalent bonds C—H, C—C, C—O, C═O, C═C, and O—H were found to be 414, 347, 351, 741, 611, and 464 kJ/mol, respectively.[10] On the basis of these values, the average complete dissociation energy of polyester and cellulose was calculated to be 443.7 and 386.2 kJ/mol, respectively. For cotton/polyester fabric, the average dissociation energy may be calculated to be 417 kJ/mol based on the ratios of cotton cellulose and polyester. Therefore, it may be concluded that polyester fabrics possess theoretically higher thermal stability than cotton/polyester blend. As a result of treatment, it is expected that some of covalent bonds are utilized to form the crosslinking chains with ZnO through the binding agent leading to a decrease in thermal stability of cotton and cotton/polyester fabrics.

The effect of treatment with ZnO formulation on the thermal decomposition behavior of cotton and cotton/

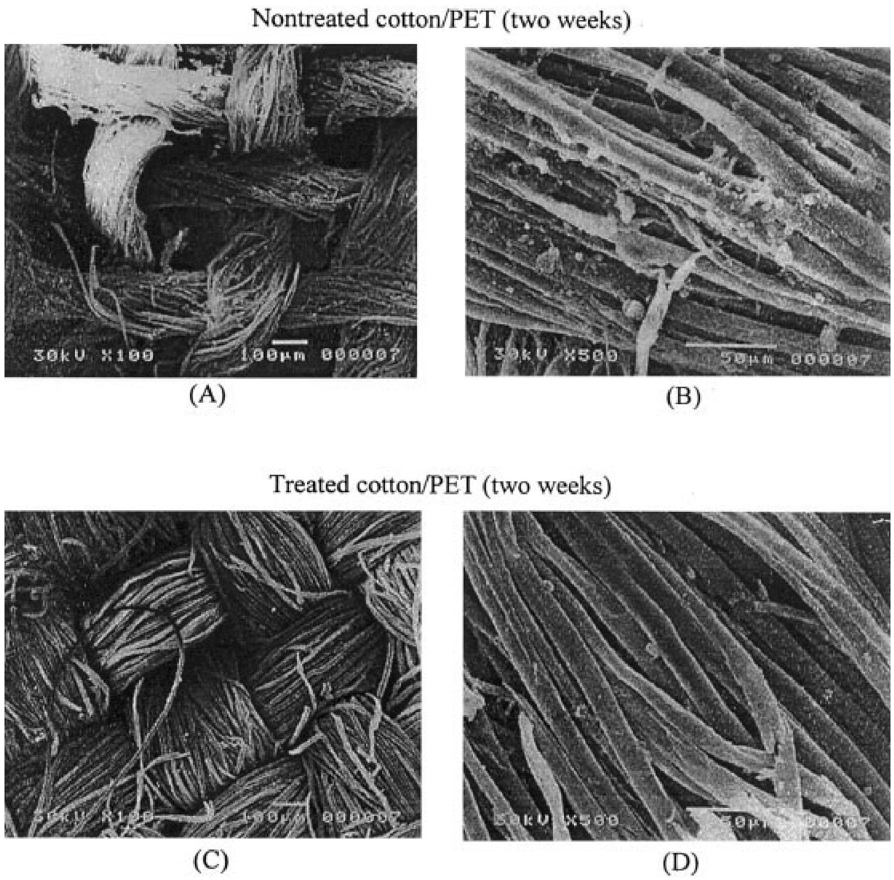

Figure 2 SEM micrographs of the surface morphology of nontreated cotton/polyester fabric (A and B) and treated cotton/polyester fabric with ZnO formulation under the effect of γ radiation at a dose of 30 kGy for antimicrobial finishing (C and D). All the fabrics were buried in an active moist soil for two weeks.

polyester was investigated by TGA as shown in Figures 3 and 4. At any event, of decomposition temperature, the different fabrics may arrange according their thermal stability as follows: Treated cotton/polyester > nontreated cotton/polyester > nontreated cotton > treated cotton. This trend can be attributed to the initially higher thermal stability of polyester component.

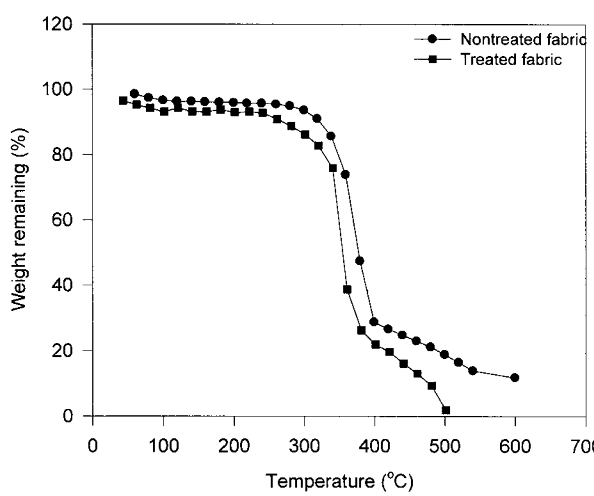

Figure 3 TGA thermograms of nontreated and treated cotton fabrics with antimicrobial ZnO formulation. Treatment conditions: ZnO, 2%; binder (Impron MTP), 2%; dispersing agent (Setamol WS), 1%; irradiation dose, 30 kGy.

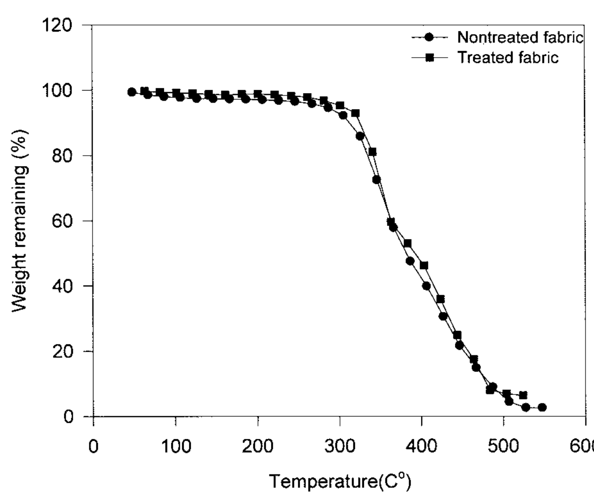

Figure 4 TGA thermograms of nontreated and treated cotton/polyester fabrics with antimicrobial ZnO formulation. Treatment conditions: ZnO, 1%; binder (Impron MTP), 2%; dispersing agent (Setamol WS), 1%; irradiation dose, 30 kGy.

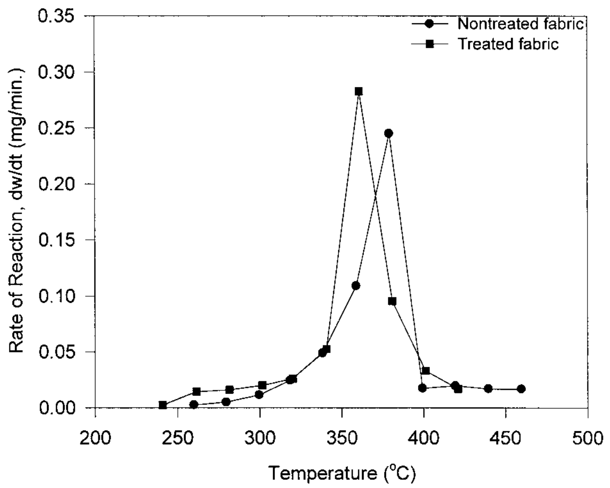

Figure 5 Rate of thermal decomposition reaction of nontreated and treated cotton fabrics with antimicrobial ZnO formulation. Treatment conditions: ZnO, 2%; binder (Impron MTP), 2%; dispersing agent (Setamol WS), 1%; irradiation dose, 30kGy.

The rate of reaction *dw/dt* or the derivative of the thermogravimetric analysis curve (DTG) taken from the initial TGA is plotted against the decomposition temperature as shown in Figures 5 and 6. It can be seen that this type of curve displays similar trends; however, the temperature of the maximum value of the rate of reaction differs from one fabric to another. Also, it can be observed that cotton fabric, either with or without treatment, expresses one maximum with increasing temperature as shown in Figure 5. As shown in Figure 6, the rate of reaction, with increasing temperature, for the nontreated or treated cotton/polyester showed multiple maxima. The maximum value of the rate of reaction for nontreated cotton fabric was seen at 379°C and that for the treated fabric was seen at 361°C, suggesting the higher stability of the nontreated cotton fabric compared to the treated one.

The rate of reaction of nontreated cotton/polyester showed the first maximum at 367°C while the treated fabric showed a first maximum at 363°C, which is probably due to the decomposition of cellulose component. The same substrates displayed a second maximum at 427 and 444°C, respectively, which they are due the decomposition of polyester component. The third maximum shown in Figure 6 for the rate of reaction of the treated cotton/polyester at 484°C is probably due to the melting point of zinc oxide element present in the formulation. In general, these observations indicate that the treated blend is thermally more stable than the nontreated fabric. The thermal decomposition of the different fabrics was further confirmed by determining the kinetics of the decomposition reaction. A method based on the rate of reaction developed by Anderson and Freeman was utilized.[11] In this method, the quantities $\Delta\log(dw/dt)$ and $\Delta\log w'$ corresponding to a constant small difference of $\Delta 1/T$ over the entire course of the initial TGA thermograms were first determined. The Anderson–Freeman equation, which relates these quantities, is given below:

$$\Delta\log(dw/dt) = n\Delta\log w - (E^*/2.303\,R)\Delta 1/T$$

Where dw/dt is the rate of reaction, w' the reactant weight, R gas constant, E^* the activation energy, and n the order of reaction. When $\Delta\log(dw/dt)$ is plotted against $\Delta\log w'$, it gives a straight line of slope n and the interception gives the activation energy E^*. The procedure and application of this method was described in previous work.[12,13] The application of this method to cotton and cotton/polyester before, and after they had been treated with the antimicrobial formulation showed the following points: (1) When $\Delta\log(dw/dt)$ was plotted against $\Delta\log w'$ for the different fabrics over the temperature scale 250–400°C, the data points do not fall on a straight line. Therefore, on the basis of the Anderson and Freeman equation, the thermal decomposition of these fabrics does not depend on residual mass, but it does depend on temperature and follows a zero order reaction. (2) The plotting of $\log(dw/dt)$ against temperature, in this case, showed a straight line and the slope will equal to $E^*/2.303\,R$, from which the activation energy can be calculated (not shown). (3) The calculated average activation energy for the thermal decomposition of nontreated and treated cotton fabrics was found to be 183.8 and 132.6 kJ/mol., respectively. (4) The average activation energy on the same basis in the case of nontreated and treated cotton/polyester blend was

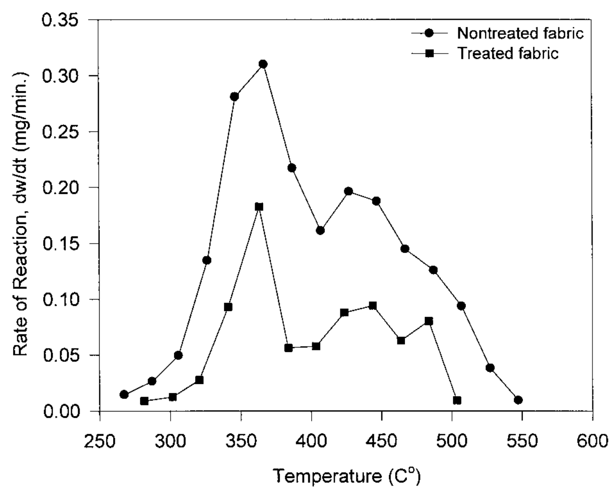

Figure 6 Rate of thermal decomposition reaction of nontreated and treated cotton/polyester blend fabrics with antimicrobial ZnO formulation. Treatment conditions: ZnO, 1%; binder (Impron MTP), 2%; dispersing agent (Setamol WS), 1%; irradiation dose, 30 kGy.

found to be 68.0 and 67.8 kJ/mol, respectively. (5) Thus, the different fabrics may be arranged on the basis of their thermal stability as follows: nontreated cotton > treated cotton > nontreated blend ≥ treated blend.

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