Antimicrobial Protection of Cotton and Cotton/Polyester Fabrics by Radiation and Thermal Treatments. I. Effect of ZnO Formulation on the Mechanical and Dyeing Properties

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ABSTRACT: Cotton and cotton/polyester fabrics were treated against microbial attack by applying a formulation based essentially on ZnO under high-energy radiation and thermal curing. To achieve the homogeneity and the reactivity of the treating formulation, a binder (Impron MTP) and a dispersing agent (Setamol WS) were used with ZnO. The antimicrobial property of the fabrics was evaluated, in terms of mechanical properties, by a soil burial test. Moreover, the effect of antimicrobial finishing on the dyeing properties in terms of color strength was investigated. It was found that the best composition that affords the best antimicrobial protection to cotton fabrics contains 2% ZnO, 2% binder, and 1% dispersing agents. For the cotton/polyester blend, the best results were achieved at the same conditions except the ZnO was 1%. It was found that the treatment under the effect of electron-beam irradiation is better than that of gamma irradiation and thermal curing. The results showed that when the finishing process was carried out before dyeing with a reactive dye, it affects the color strength rather than performing the finishing after the dyeing process. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 1129–1137, 2003

Key words: microbial resistance; crosslinking; radiation; mechanical properties; cotton; blends

INTRODUCTION

Textiles for outdoor use are constantly exposed to the influence of microbes, in which the formation of spots and odors are just the perceivable signs of contamination. When fibers are subjected to attack by microbes, specific properties such as tensile strength and impermeability are lost. Textile clothing for work, sports, and military use is particularly susceptible to microbial attack in which soil and perspiration offer ideal living conditions for microbes.

Extensive research work and patents have dealt with a wide range of organic compounds as fungicides for textile materials such as the interaction products of *N*-cetylpyridinium bromide and thiols together with binders,[1,2] 2,4,4′-trichloro-2′-hydroxydiphenyl ether,[3] 2-(carbomethoxyamino)benzimidazole,[4] polyhexamethylenebiguanide,[5,6] and cyclodextrinhiba oil.[7] Also, solutions containing binders, dispersing agents, and metallic salts have been widely applied to textile materials as active bactericides and fungicides and have been reported as patents in the literature.[8–12] In all these works, it was reported that the binding and dispersing agents are the determining compounds in performing successfully antimicrobial treatment of textile materials. In previous reports, cyanoric chloride[13] and the commercial compound Sandospace R[14] were used as combining agents in the field of dyeing textile fabrics.

Zinc oxide, as an inorganic material, is stable to heat, which makes it possible to maintain its functional property permanently and not change color and oxidation compared to copper and silver. Moreover, it is nontoxic to the human body compared to organic antimicrobial agents. In this regard, it has been reported as an antibacterial, deodorizing, and UV-absorbing agent for fabrics and films of polymers.[15]

In the present study, an antimicrobial formulation containing ZnO and binding and dispersing agents was used to protect cotton and cotton/polyester fabrics against a broad spectrum of microbes. This formulation was applied to these fabrics under high-energy radiation and thermal curing. The antimicrobial properties were evaluated in terms of the retention in the mechanical properties after burying in a soil rich in microorganisms. Moreover, the effect of

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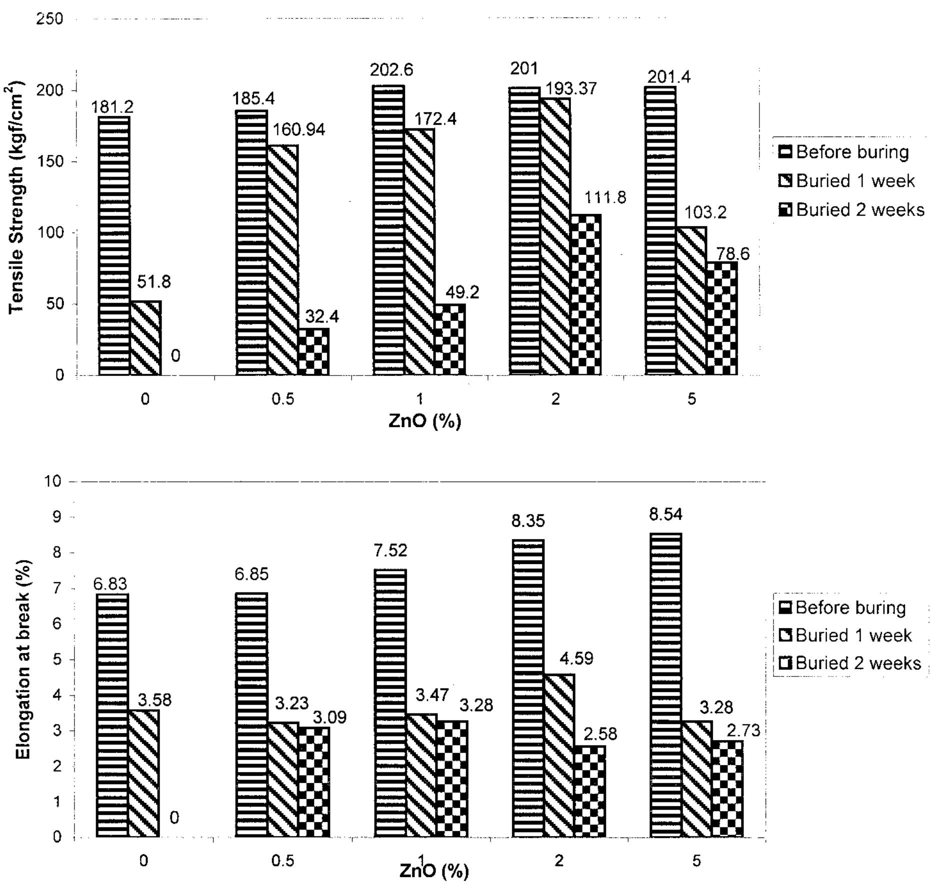


Figure 1 Mechanical properties of cotton fabrics treated with antibacterial formulations containing various contents of ZnO under gamma radiation after soil burial test. Treatment conditions: binder (Impron MTP), 2%; dispersing agent (Setamol WS), 1%; irradiation dose, 30 kGy. All concentrations of the reagents are based on the volume of the treating formulation.

these treatments on the dyeing properties was investigated.

EXPERIMENTAL

Materials

Plain-weave cotton and cotton/polyester blend fabrics were kindly supplied by the 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 not subjected to any finishing processes. It is to 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 5 g/L Na_2CO_3 and 2 g/L detergent at 60^0C to remove any undesired materials. A fine powder of ZnO of analytical grade was kindly supplied by Prolabo (Prolabo, Cedex, France). The Impron MTP binding agent and Setamol WS as a dispersing agent were kindly supplied by Clariant (Germany) and BASF (Ludwigshafen, Germany), respectively. Impron MTP is a low-viscosity aqueous dispersion of about 50–200 mPa s at 20°C and it is a self-crosslinking acrylate-based copolymer. Setamol WS is a brownish microgranule anionic dispersing agent and it is a product of condensation of an aromatic sulfonic acid. The reactive dye Levafix Blue, used throughout this work, was kindly supplied by Bayer (Germany).

Treatment of textile fabrics with ZnO formulation

The appropriate quantities of ZnO and binding and dispersing agents were continually stirred until the ZnO was homogeneously dispersed. Cotton or cotton/polyester strips (30 $\times$ 6 cm) were impregnated in this dispersion for 5 min. The samples were then squeezed to a pick up of $\sim$100%, air-dried, and, afterward, subjected to fixation by thermal or radiation techniques. Irradiation to the required doses was carried out in a Co-60 gamma cell at a dose rate of 0.276 kGy/h. The samples for thermal curing were treated first with the ZnO formulation and then placed in an oven at 160°C for different periods.

Evaluation of microbial resistance

The microbial resistance of the treated fabrics was tested by a soil burial test.[16] In this method, naturally

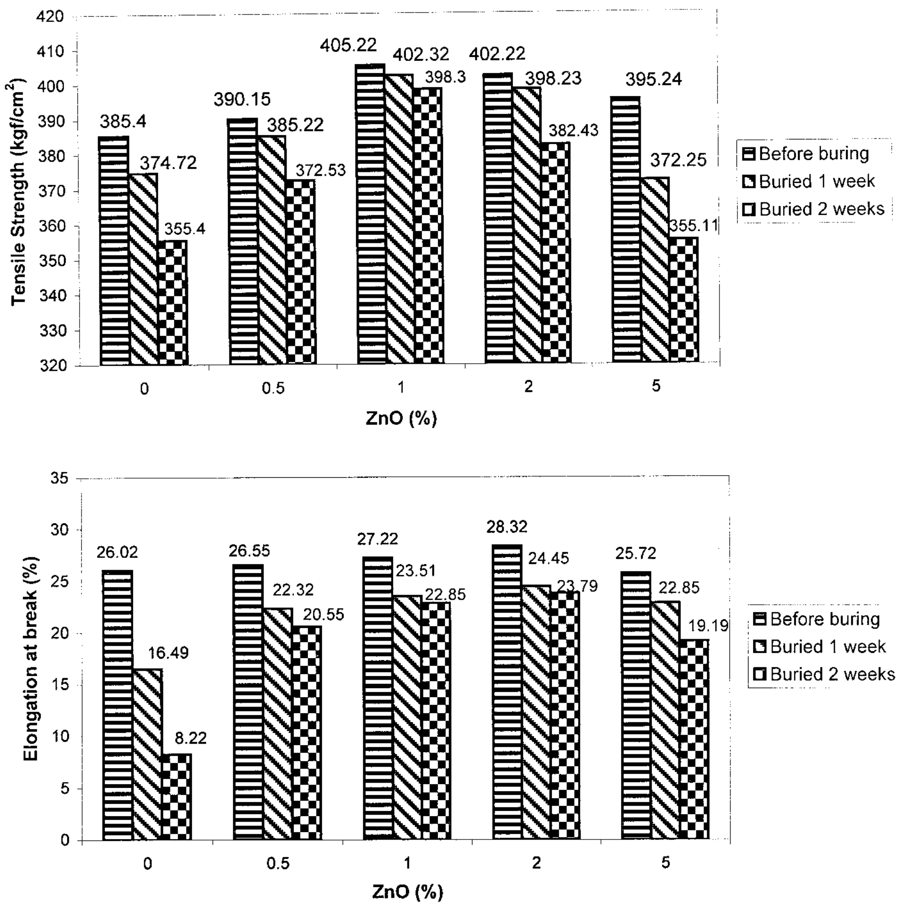


Figure 2 Mechanical properties of cotton/polyester fabrics treated with antibacterial formulations containing various contents of ZnO under gamma radiation after soil burial test. Treatment conditions: binder (Impron MTP), 2%; dispersing agent (Setamol WS), 1%; irradiation dose, 30 kGy. All concentrations of the reagents are based on the volume of the treating formulation.

fertile top soil is placed in a dry wooden box to a depth of at least 13 cm. The soil was brought to the optimum moisture content by gradual addition of water accompanied by mixing. The soil was left for 24 h and then it was sieved through a 6.4-mm mesh screen. A uniform moisture content was maintained by covering the soil container with a suitable lid. The moisture content of the soil during the test period was maintained between 20 and 30% (based on the dry weight) and the temperature was kept at 28°C during the burying of the samples. Before burying, the treated samples were first wet out (but not rubbed or squeezed) with an aqueous solution containing 0.05% of a nonionic wetting agent. The specimens were then buried horizontally. Precautions were taken to ensure uniform covering with the soil along the length of the fabric strips.

Mechanical properties

The buried samples were gently washed and air-dried at room temperature for 24 h before measuring the tensile strength. The stress–strain behavior of the samples was determined using an Instron tensile tester (Model 1195). The testing was carried out at room temperature, employing a strain rate of 10 mm/min. All recorded data are the average of five measurements.

Dyeing procedure

The bath of the reactive dye was prepared by dissolving 2 wt % (based on fabric weight) and 10 g/L sodium carbonate (Na_2CO_3) in hot water. The samples were dyed according to a procedure described elsewhere.[17]

Color-difference measurements

A microcolor unit attached to a data station manufactured by Dr. Lang (Germany) was used for the color-strength measurements. In this system, the L^* value specifies the dark–white axis; a^*, the green–red axis, and b^*, the blue–yellow axis. The recorded value of the different color interceptions is the average of five rep-

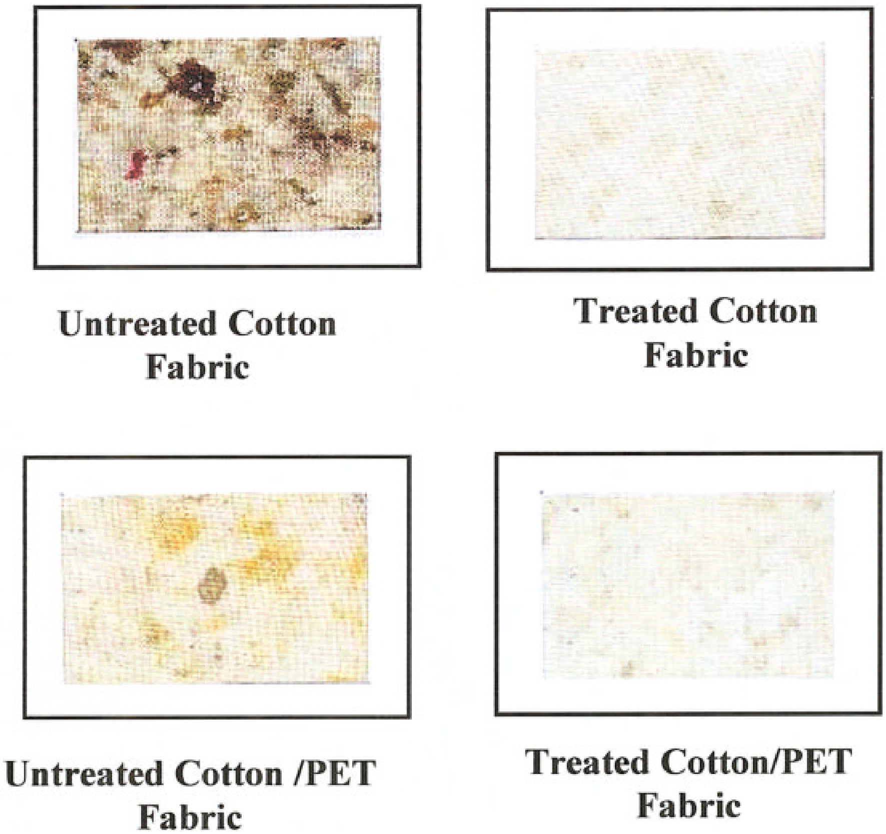


Figure 3 Photographs of cotton and cottton/polyester fabrics before and after they had been buried in a moist soil rich in microorganisms for 10 days. Treatment conditions: ZnO, 1%; binder, 2%; dispersing agent, 1% gamma irradiation dose, 3 Mrad. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

licate measurements. The color difference ΔE^* was calculated according to the following equation:

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

RESULTS AND DISCUSSION

In the present work, a method was used based on the covering and coating of the fibers with a formulation that chemically bonded to form an active barrier against the growth of microorganisms. The chemical bonding between the fibers and coating was conducted under gamma irradiation. Tensile mechanical properties of natural fibers, unlike synthetics, are severely affected by the attack of insects, bacteria, rot, fungi, etc. The different factors that may affect the efficiency of antibacterial finishing, in terms of tensile properties, such as irradiation dose, binder, and ZnO concentration, were investigated.

Antimicrobial finishing by radiation treatment

Effect of ZnO agent

The tensile mechanical properties of cotton and cotton/polyester fabrics treated with antimicrobial formulations containing different contents of ZnO under gamma irradiation are shown in Figures 1 and 2. It is to be noted that the contents of the binder (Impron MTP) and the dispersing agent (Setamol WS) were kept constant, at 2 and 1%, respectively. Also, the irradiation dose was kept constant at 30 kGy. Before burying, it is clear that the application of the antimicrobial formulation with increased ZnO content increases the tensile strength of the cotton and cotton/polyester fabrics. This behavior may explained on the principle of sizing materials used to strengthen the strings against friction during the weaving process of textiles. In a similar manner, the ZnO formulation under gamma irradiation forms a thin layer of coating around the fibers and thus resists the stress tension. Also, the elongation to break was found to slightly increase with increasing ZnO content. These trends may be interpretated on the basis that the application of the ZnO formulation improves the surface of the fibers through the formation of thin layers. As shown in Figure 2, the effect on tensile strength properties of cotton/polyester fabrics is less than those in cotton fabrics at the same condition of ZnO contents and buring.

At the end of the 1-week burial test, a great reduction in tensile strength of the untreated cotton fabrics

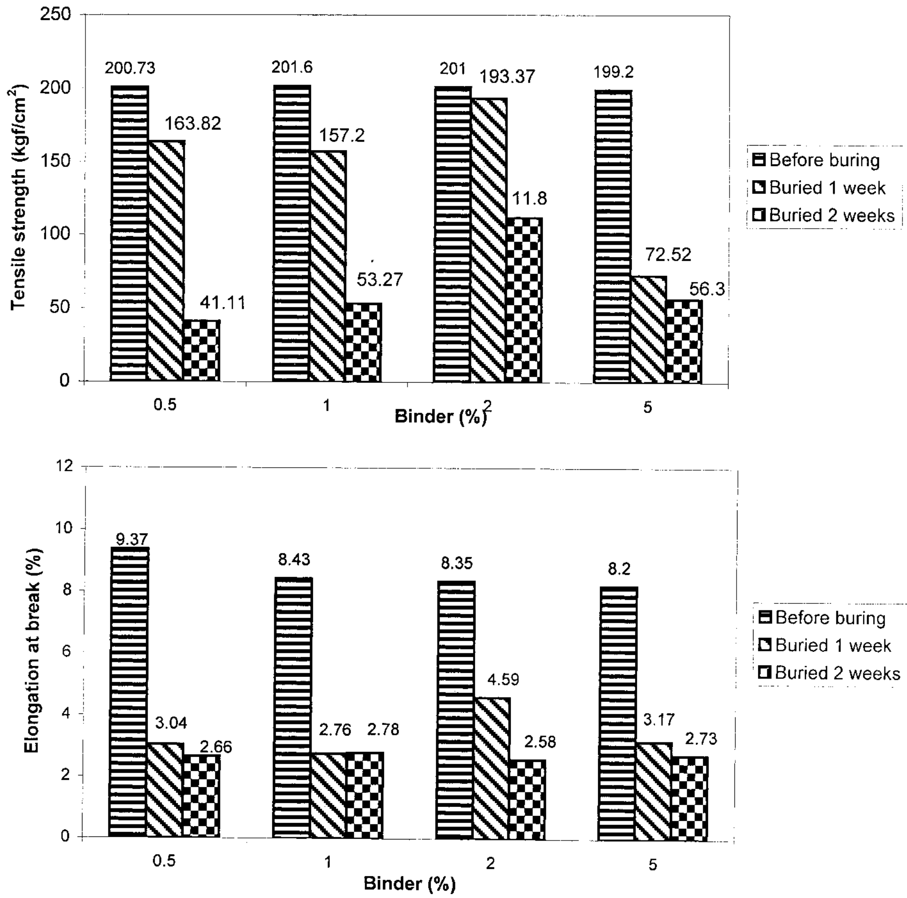


Figure 4 Mechanical properties of cotton fabrics treated with antibacterial formulations containing various contents of binder (Impron MTP) under gamma radiation after soil burial test. Treatment conditions: ZnO 2%; dispersing agent (Setamol WS), 1%; irradiation dose, 30 kGy. All concentrations of the reagents are based on the volume of the treating formulation.

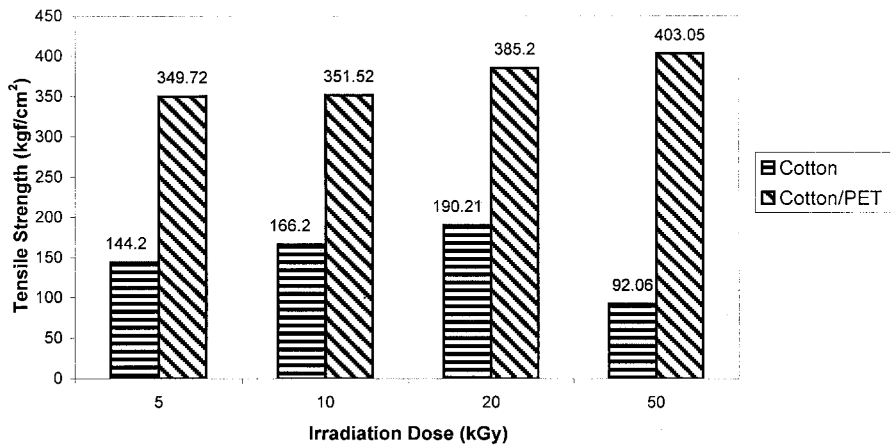
can be observed from 181 to 52 kgf/cm^2. After 2 weeks, the untreated samples were completely attacked by microorganisms so that they could not be tested for mechanical properties. These findings are very clear from the photographs taken for this sample as shown in Figure 3. The sample was covered with large brown patches and black, yellow, and orange spots and it was hard, of moldy odor, and very slimy to the touch when wet or drying. Also, it had a brittle feel and was obviously thinner than before burial.

It is clear that the protection of cotton fabrics, in terms of tensile strength, against microbes, fungi, and bacteria increases with increasing ZnO contents, particularly at 2%. At this content, the treated cotton fabrics still retain ~96 and 55% of their tensile strength at the end of 1 and 2 weeks in soil, respectively. The elongation-to-break point was found to decrease with an increasing period of the burial test.

As shown in Figure 2, the tensile strength of the untreated cotton/polyester blend is much higher than that of the cotton fabrics. Also, the application of the antimicrobial ZnO formulation to the cotton/polyester blend is shown to increase the tensile strength with approximately the same amount as it does in the case of the cotton fabrics. Unlike the cotton fabrics, the cotton/polyester blend possesses a higher resistance to microorganisms than that of the cotton fabric, even the untreated sample. This behavior can be attributed to the presence of the synthetic polyester component at a high ratio with respect to the natural cellulose which is originally more susceptible to microorganisms. On the basis of the data on Figure 2, it can be concluded that ZnO at a ratio of 1% is suitable to afford the best protection against microorganisms. This is because an increase of ZnO content beyond this ratio seems to cause an opposite effect compared to the untreated samples. Similar trends can be observed in the case of elongation to break.

Effect of binding agent

Binders are low-viscosity, mostly acrylate, copolymers which polymerize or condense into a network structure under the effect of heat or radiation with a sufficiently high elastic modulus and comparatively small elongation. Figure 4 shows the tensile mechanical properties of cotton fabrics treated with antimicrobial formulations containing various contents of the binder



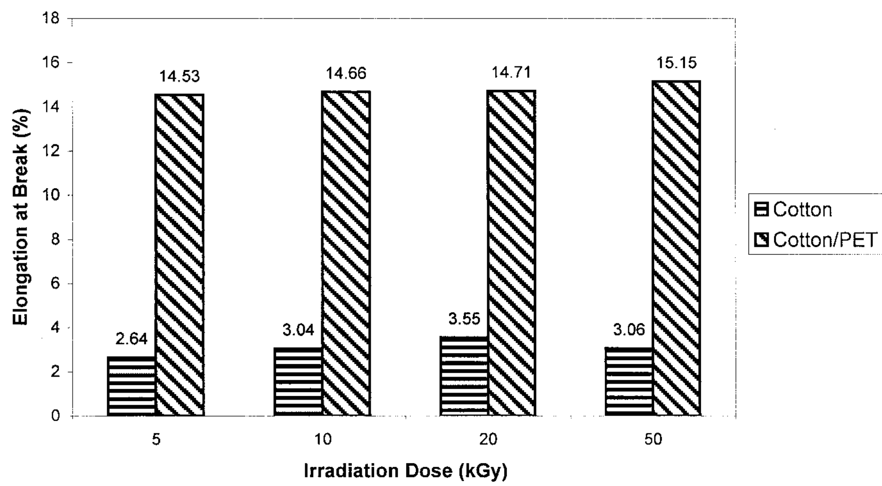


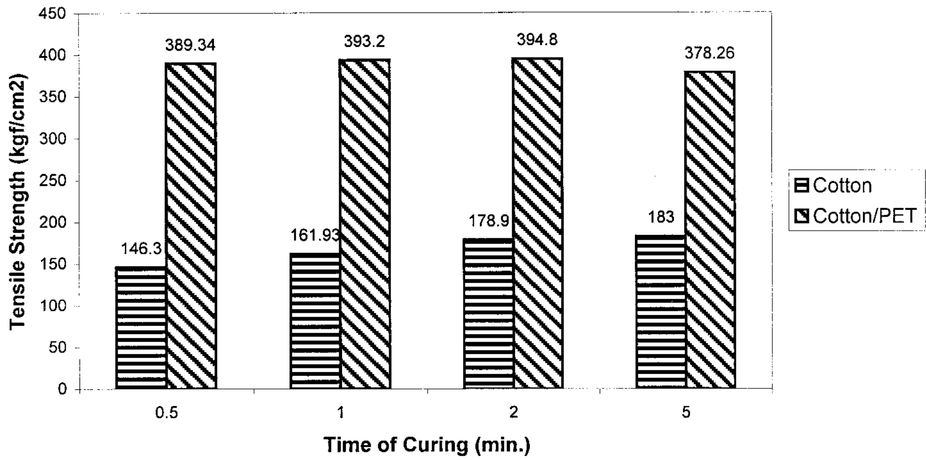
Figure 5 Mechanical properties of cotton fabrics treated with antibacterial ZnO formulations under the effect of various doses of accelerated electrons at the end of soil burial test for 10 days. Treatment conditions: ZnO 2%; binder (Impron MTP), 2%; dispersing agent (Setamol WS), 1%; irradiation dose, 30 kGy. All concentrations of the reagents are based on the volume of the treating formulation.

(Impron MTP) under gamma irradiation before and after the soil burial test. It should be noted that the contents of the other agents, ZnO and the dispersing agent (Setamol WS), were kept constant at 2 and 1%, respectively. Apparently, the increase of the binder content has no effect on the tensile strength up to 2%, even though a higher content of 5% tends to cause a slight reduction in the tensile strength. In fact, the relatively higher tensile strength of the treated fabrics compared to the untreated one is due to the presence of ZnO originally in the formulation. The effect of the binder as a combining agent, however, appears clearly after the samples had been buried in the soil. At the end of the 2-week burial test, cotton fabrics retain higher amounts of their tensile strength with increasing binder contents rather than with increasing ZnO contents, as shown in Figure 1. Meanwhile, it is indicated that a content of 2% of the binder in the formulation is appropriate to afford the best antimicrobial effect.

Antimicrobial finishing by electron-beam irradiation

Accelerated electrons generated from electron-beam accelerators have been now successfully applied in many industrial fields covering the surface curing of coatings, paints, grafting, flue gas treatment, polymer modification, sterilization, and food preservation. However, accelerated electrons are characterized with a high dose rate compared to gamma radiation.

Figure 5 shows the tensile mechanical properties of cotton and cotton/polyester fabrics treated with antimicrobial formulations under the effect of various doses of accelerated electrons at the end of 10 days of the burial test. It should be noted that the treatments were performed at the same conditions of gamma radiation. In comparison with the data of gamma radiation, a few points may be made: (1) The retention in tensile strength of the cotton fabrics was found to increase with an increasing electron-beam irradiation



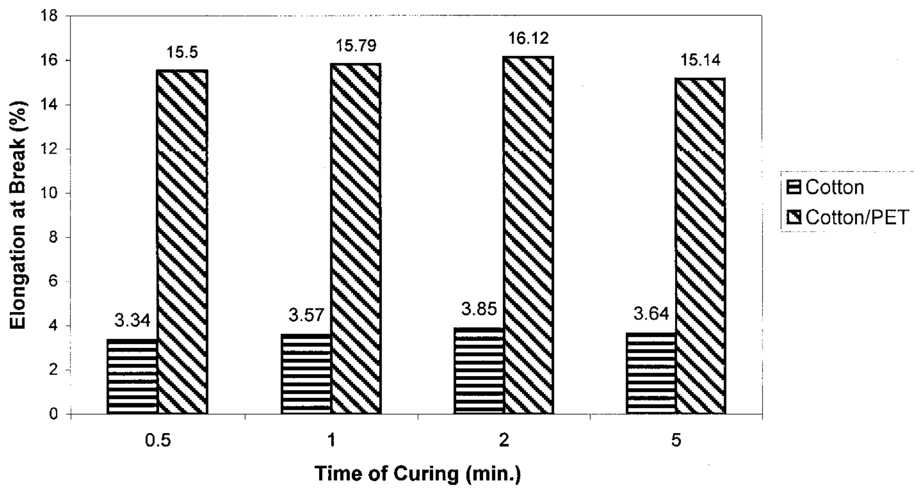


Figure 6 Mechanical properties of cotton/polyester fabrics treated with antibacterial ZnO formulations under the effect of thermal curing at 160°C and different periods at the end of soil burial test for 10 days. Treatment conditions: ZnO 2%; binder (Impron MTP), 2%; dispersing agent (Setamol WS), 1%; irradiation dose, 30 kGy. All concentrations of the reagents are based on the volume of the treating formulation.

dose up to 30 kGy and then tended to decrease at high doses of 50 kGy. (2) In the case of the cotton/polyester blend, the retention in tensile strength was found to increase with an increasing irradiation dose. (3) At any irradiation dose, the retention in tensile strength of either the cotton fabric or its blends with polyester treated with the electron beam is relatively higher than those treated with gamma radiation. (4) The elongation-to-break point after the burial test was not greatly influenced by the type of radiation.

Antimicrobial finishing by thermal treatment

The thermal curing technique is usually used to finish natural and synthetic fabrics to add desired properties such as wash–wear and durable press to cotton fabrics with formaldehyde or aminoformaldehyde resins. However, to perform this process, a metal catalyst should be added to the finishing formulation to achieve the crosslinking of formaldehydes with cellulose. In the present study, cotton and a cotton/polyester blend were treated with the previous antimicrobial formulation under thermal curing at 160°C for various periods. These treated samples were subjected to the soil burial test for 10 days and the tensile mechanical properties were tested as shown in Figure 6. It is clear that the retention in tensile strength of the cotton or cotton/polyester fabrics increases gradually with an increasing time of thermal curing up to 5 min.

On the basis of the different methods used for applying the antimicrobial formulation, a few points can be made: (1) The higher retention in tensile strength for cotton fabrics by applying accelerated electrons was ~190 kgf/cm^2 at a dose of 30 kGy. (2) The highest retention by applying thermal curing was ~183 kgf/cm^2 at a temperature of 160^{0}C for 5 min. Therefore, it may concluded that electron-beam irradiation is better than is thermal curing for cotton fabrics. (3) The high-

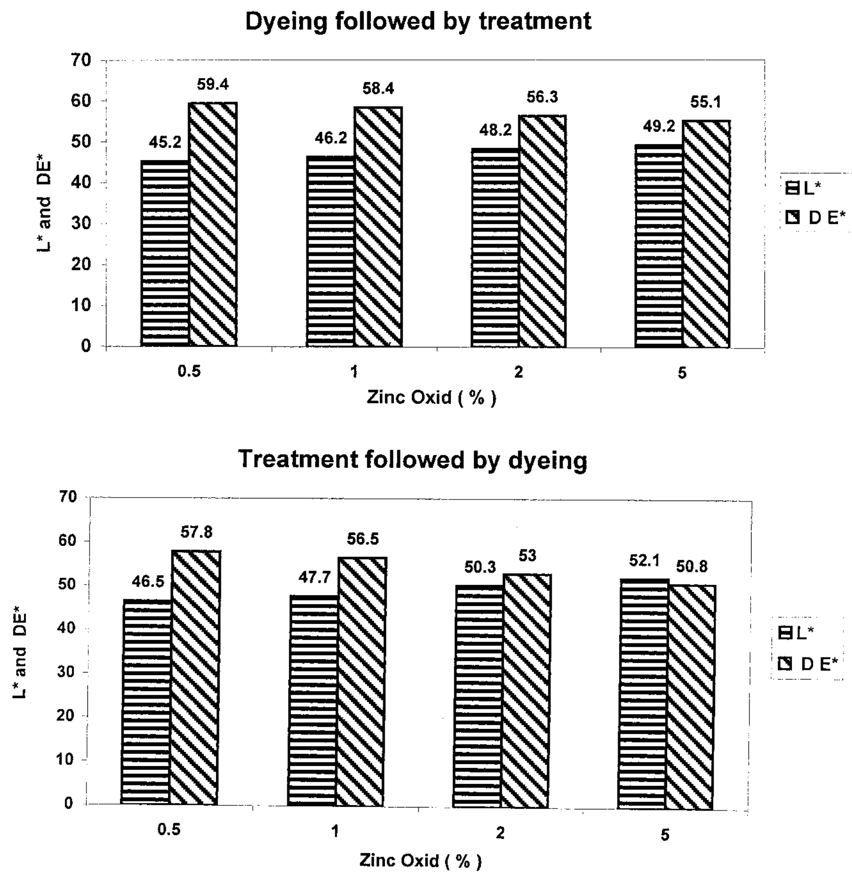


Figure 7 Effect of antibacterial finishing of cotton fabrics with formulations containing various concentrations of ZnO under gamma irradiation on the color strength (*L**) and difference (*DE**) before and after they had been dyed with the reactive dye Levafix Blue. Treatment conditions: binder (Impron MTP), 2%; dispersing agent (Setamol WS), 1%; irradiation dose, 30 kGy. All the reagents are based on the volume of treating formulation. Dye concentration, 2% (based on fabric weight) in all cases.

est retention in tensile strength for the cotton/polyester blend by applying electron-beam irradiation was ~403 kgf/cm^2 at a dose of 40 kGy, while the highest retention by applying thermal curing was ~395 at a temperature of 160^{0}C for 2 min. (4) The treatment with electron-beam irradiation or thermal curing has nearly no effect on the elongation to break of cotton or cotton/polyester fabrics.

Effect of antimicrobial finishing on dyeing properties of cotton fabrics

As much as is the need to protect textile fabrics from microbial attack, they still require dyeing treatment to give the fabric or garment the appearance which make them attractive to the consumer. In the present study, an attempt was made to investigate the effect of antimicrobial finishing on the dyeing properties of cotton fabrics before and after treatment with the ZnO formulation.

Figure 7 shows the effect of antimicrobial formulations with increased ZnO content under gamma radiation on the color strength and difference of cotton fabrics dyed with a reactive dye (Levafix Blue) before or after treatment. It is well known that cotton cellulose fibers are hydrophilic in nature and have a direct affinity for direct and reactive dyestuffs because of the presence of the hydroxyl groups attached to every repeating glucoside unit. Therefore, the measured color difference ΔE^* for the untreated cotton fabric dyed with the reactive dye was found to be 59.6. This value is based on the color strength L^* of the control sample of 94.1 (untreated and undyed). It is clear that the color difference ΔE^* of the cotton fabrics decreases with an increasing content of ZnO in the formulation whether the samples were dyed before or after finishing. However, the color differences ΔE^* values of the cotton fabrics dyed after finishing is lower than of those dyed before finishing at any ZnO content. Based on the above findings, a few points can be: (1) The finishing step with ZnO, whether it is carried out before or after dyeing, has an acceptable effect on the color strength of the cotton fabrics. In this regard, the decrease in the color difference ΔE^* by increasing the ZnO content from 0.5 to 5% in the case of cotton fabrics dyed before finishing was calculated to be 4.3, while that for the samples dyed after finishing was 7.0.

(2) The finishing step causes a relatively adverse effect on the dyeing properties of cotton fabrics when it is performed before dyeing. (3) Since increase of the ZnO content of more than 2% does not greatly enhance the protection against microbial attack (Fig. 1), the decrease in color strength at this level, thus, is acceptable. (4) The decrease in color strength can be explained on the basis that some hydroxyl groups of cellulose fibers were hidden or blocked for the reactive dye.

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