

Efficiency of Ultraviolet/Ozone Treatments in the Improvement of the Dyeability and Light Fastness of Wool

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ABSTRACT: In this study, we evaluated the effect of ultraviolet/ozone treatments for different times on the characteristics of wool fabrics with respect to wettability, permeability, yellowness index, and weight loss. The beneficial effects of this treatment on dyeability, color parameters, light fastness characteristics, and the change in color difference after exposure of the treated dyed samples to artificial daylight for about 150 h was investigated. The results indi-

cated that the improvement in wetting processes may have been due to surface modifications; this meant that an increase in the amorphousness of the treated samples, the oxidation of the cystine linkage on the surface of the fabrics, and the formation of free-radical species encouraged dye penetration and aggregation inside the fiber pores as well as bond formation. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 3668–3675, 2003

INTRODUCTION

Because of increasing environmental legislation relating to adsorbable organohalogen (AOX), recent work has focused on the development of dry treatments^{1–4} for the modification of fabric surfaces to achieve good dyeability and excellent fastness properties. Thus, the application of ultraviolet (UV)/ozone treatments for cleaning surfaces was well reviewed by Vig and others.^{1,5} A good oxidative efficiency can be achieved by the coupling of UV radiation and ozone. UV/ozone treatments are essentially a photosensitized oxidation process in which surface molecules are excited and/or dissociated by the absorption of short-wavelength UV radiation.

Generally, the exposure of textiles to a source of radiant energy produces deleterious changes in the physical and chemical properties, with the extent depending on the conditions of exposure and the chemical nature of the fibers.^{6–8} For wool, its complexity is illustrated by the different important chemical groups it contains and the intermolecular forces of attraction that are formed.^{8–12} First, there are the polar peptide groups (i.e., —CO—NH—). Second, the oxygen of the carbonyl groups (—CO—) is slightly negatively charged and, as a result, will form hydrogen bonds with the slightly positively charged hydrogen of the imino groups (—NH—) of other peptide groups. Third, cystine, the sulfur-containing amino acid capable of forming disulfide crosslinking tends towards greater chemical stability, resulting in less dye absorp-

tion. Also, this cystine linkage is sensitive to chemical attack and is removed and/or modified by aqueous chlorination and high radiant energy. Also, the very absorbent nature of wool is caused by the polarity of the peptide groups, the salt linkages, and the amorphous nature of its polymer system. In this study, the effect of UV/ozone treatments of wool were evaluated through the study of wettability, weight loss, and the yellowness index of the fabrics. Also, the study was extended to investigate the effect of such treatment on the dyeing properties and light fastness (LF) characteristics by the application of two different classes of dye.

EXPERIMENTAL

Materials

Pure wool fabrics (100%, weight = 137 g/m², thickness = 0.35 mm) were used in this study and were supplied by Goldentex Co. (Cairo, Egypt). The fabric was used without any purification.

Two different dye classes were used: (1) a direct dye, solophenyl orange (TGL 182 %) C.I. 34, and (2) a reactive dye, Levafix Brilliant Red (E4-BA) C.I. 158. These dyes were kindly supplied by Ciba Geigy Co. (Cairo, Egypt).

UV/ozone treatment

The samples were treated with a UV/ozone source. A high-intensity, low-pressure mercury lamp without an outer envelope (LRF02971, 400 W, 220 V, Poland) was placed in a closed box of diameter 60 × 60 × 60 cm³, and the samples were put around the source at a distance of 20 cm.

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Atomic oxygen⁵ is generated when molecular oxygen is subjected to radiation with a high intensity. The product of this excitation is the formation of simple volatile molecules, that is, ozone, which is absorbed by the surface of most hydrocarbons. The wool samples were exposed for different periods ranging from 20 to 120 min.

Wettability

Fabric wettability was determined by the measurement of the time required for the treated samples to absorb 0.5 mL of distilled water.

Air permeability measurements

The air permeability of the treated samples, which was taken as a measure of the change in porosity during the different treatment times, was measured. These measurements were carried out according to an ASTM¹³ standard method with an air permeability tester Fx 3300 (Switzerland).

Weight-loss determination

The determination of the weight loss was made on treated samples at about 20°C and 65% relative humidity. The results are expressed as the percentage of the weight loss of the treated samples compared with the untreated samples with the following formula:¹⁴

$$\text{Weight loss\%} = \frac{W_t - W_i}{W_i} \times 100$$

where w_t is the weight of the treated samples at different treatment periods and w_i is the weight of the untreated (blank) samples.

Yellowness index determination

The degree of yellowness of the treated samples was measured and evaluated according to ASTM D1925 with an Optimatch 3100 spectrophotometer (United Kingdom), where for each sample, the mean values of three measurements were taken.

Dyeing procedure

The treated samples were dyed with the exhaustion dyeing method in a laboratory dyeing bath. For the two dyes being tested, the liquor ratio used throughout the study was 1:50. The dye concentration was 1% of weight fabric (owf) and the pH of the dyeing media was about 7. Dyeing was conducted for 45 min at 60°C.

Color measurements

The color strength (K/S) values of the treated dyed samples were evaluated from the reflection spectra at the proper wavelength of the color being tested with the Kubelka Munk equation.¹⁵ Also, for the evaluation of the tristimulus values X , Y , and Z , the reflection spectra in the visible range 400–700 nm of all of examined samples were measured. These tristimulus values were used to calculate the three color parameters [L , a , and b where L refers to lightness–darkness with values from 100 to 0 representing white to black, respectively; a values run from negative (green) to positive (red); and b values run from negative (blue) to positive (yellow)] and also the color difference (ΔE); the details of these parameters are clarified in the Results and Discussion section.

Light exposure and LF evaluation

The dyed samples treated with a standard blue scale were exposed to artificial daylight with a Tera LF tester (Academy of Scientific Research, Egypt),¹⁶ at a temperature of $25 \pm 2^\circ\text{C}$ and a relative humidity of $65 \pm 5\%$. The exposure was continued until the blue scale number 7 showed a slight change, after about 150 h. Thus, the LF was assessed visually according to an ASTM¹⁷ standard method.

RESULTS AND DISCUSSION

Because the wool fiber surface plays an important role in the dyeability,^{1,5,18,19} the LF characteristics, and color parameters, the effects of surface modification via the application of UV/ozone treatment for different exposure periods were thoroughly examined and evaluated by consideration of the change in physical properties such as wettability, permeability, weight loss percentage, and yellowness index, as shown in Table I. The wetting of wool fabrics is a sensitive indication of surface modification; the results indicated that the wetting times greatly decreased with increasing treatment times and reached a minimum value (higher wettability) at 100 min of exposure; that is, an increase wettability may have been due to the oxidation of the cystine content on the surface of the wool fabrics, which is responsible for its hydrophobic nature and limited wettability and dyeability, forming cysteic acid and thus modifying or volatilizing the surface lipids.^{1,18,19} The UV/ozone treatments of the fibers became more hydrophilic; this could be expected to improve the dyeability. This trend agreed well with the permeability measurements, which were taken as a measure of the change in the porosity of the fabrics under the effect of the change in treatment times.

In summary, the improvement in both the wettability and permeability of the treated fabrics, led to an

TABLE I
Effect of UV/ozone Treatment for Different Times on Some of the Physical Properties of the Wool Fabrics

Treatment time (min)	Weight loss (% \cdot G/m ²)	Air permeability (cm ³ /cm ² /s)	Wettability (s)	Whiteness index	Yellowness index
0	—	154.2	1080	33.47	12.53
20	22.6	154.9	300	28.24	17.33
40	-22.2	157.7	300	24.77	19.27
60	-25	158.9	300	21.81	21.15
80	-29.4	161.4	240	17.28	24.69
100	-11.6	162.5	150	11.80	29.52
120	-23.4	150.1	210	13.17	28.36

increase in their swellability during wetting processes, which increased their dyeability and the aggregation of the dye molecules inside the fiber pores and produced an enhancement in the LF.

When the change in weight loss during the different treatment times is considered,¹⁴ which was taken as a measure of the significant damage that occurred, the results indicate that there was an increase in weight during the first treatment period (20 min) followed by an increase in weight loss percentage, which reached a minimum value at 100 min of exposure (-11%). This weight loss may have been due to the effect of the UV/ozone treatment on the surface of the wool fabrics; that is, surface oxidation occurred, creating polar groups and modifying or volatilizing the surface lipids.^{1,20}

Yellowness index

The results of Table I demonstrate that with increasing treatment times, the yellowness increased. Immediately after treatment, especially after longer treatment periods, the wool was a greenish color, which gradually changed to yellow. This greenish color was probably due to the formation of cystyl radicals.¹ The observed increase in yellowness may have been due to the analysis of photolabile amino acids, such as^{11,21,22} cystine, tryptophan,¹¹ and tyrosine, to yield colored species on exposure to UV/ozone; thus, the yellow-

ness index increased. However, yellowing in the surface layer may protect fabrics to some extent against photodegradation in the cortex¹⁰ and is also associated with changes in the wavelength range 300–400 nm.

K/S and the absorption coefficient (α)

The results in Tables II and III indicate that UV/ozone treatments increased the dyeability, which is represented by the K/S values. This continuous improvement in dyeability as a result of increasing treatment times may have been due to the following: the increase in wettability and permeability were a direct measure for the increasing porosity²³ of the treated fabrics; thus, the exhaustion of the dye to the fabric surface increased, and this led to enhanced dyeability. Also, the activation of the fibre surface via the oxidation of the cystine linkage and the formation of free-radical species within the fiber gave covalent bonds a chance to form between the dye and the fiber. However, the higher dyeability of the reactive dye compared with the direct dye, because the photooxidation of cystin is reported to produce an increase in thiol group content,^{1,10,18–20} which is known to exhibit higher reactivity toward the reactive dye, led to covalent bond formation.

The results of the dyeability were manifested through the evaluation of α in the visible range at different treatment times from the equation:

TABLE II
Effect of UV/Ozone Treatment for and Different Times on the Dyeability, Color Parameters (L , a , and b), $\Delta E'$, and LF Values of the the Wool Fabrics Dyed with the Direct Orange Dye

Treatment time (min)	K/S	L	a	b	$\Delta E'$	LF
0	1.27	73.12	5.10	22.47	10.23	4
20	2.65	70.22	9.53	35.99	15.17	5
40	6.99	66.89	18.18	53.92	14.87	5
60	7.99	66.03	18.81	55.38	15.54	5–6
80	11.84	64.44	22.20	61.66	15.13	6
100	17.06	62.57	27.58	67.25	15.96	6
120	15.87	62.44	26.57	65.76	16.24	6

TABLE III
Effect of UV/Ozone Treatment and for Different Times on the Dyeability, Color Parameters (*L*, *a*, *b*), the $\Delta E'$, and LF Values of the Wool Fabrics Dyed with the Reactive Red Dye

Treatment time (min)	K/S	<i>L</i>	<i>a</i>	<i>b</i>	$\Delta E'$	LF
0	2.66	56.73	33.71	2.13	4.56	4-5
20	11.22	46.59	50.28	10.71	1.93	6
40	17.33	43.68	53.28	15.27	—	7
60	19.17	42.43	53.33	17.20	—	7
80	23.76	40.90	54.57	20.95	—	7
100	26.94	39.51	54.42	23.11	—	7
120	27.74	38.97	54.38	24.52	—	7

$$\alpha = (1/d) \ln R$$

where *d* is the thickness of the fabric and *R* is the reflection percentage. Such results are represented in

Figures 1 and 2. It was clear that a characteristic band at definite wavelength for each dye under testing appeared and the α values increased with increasing treatment times and reached a maximum at 100 min.

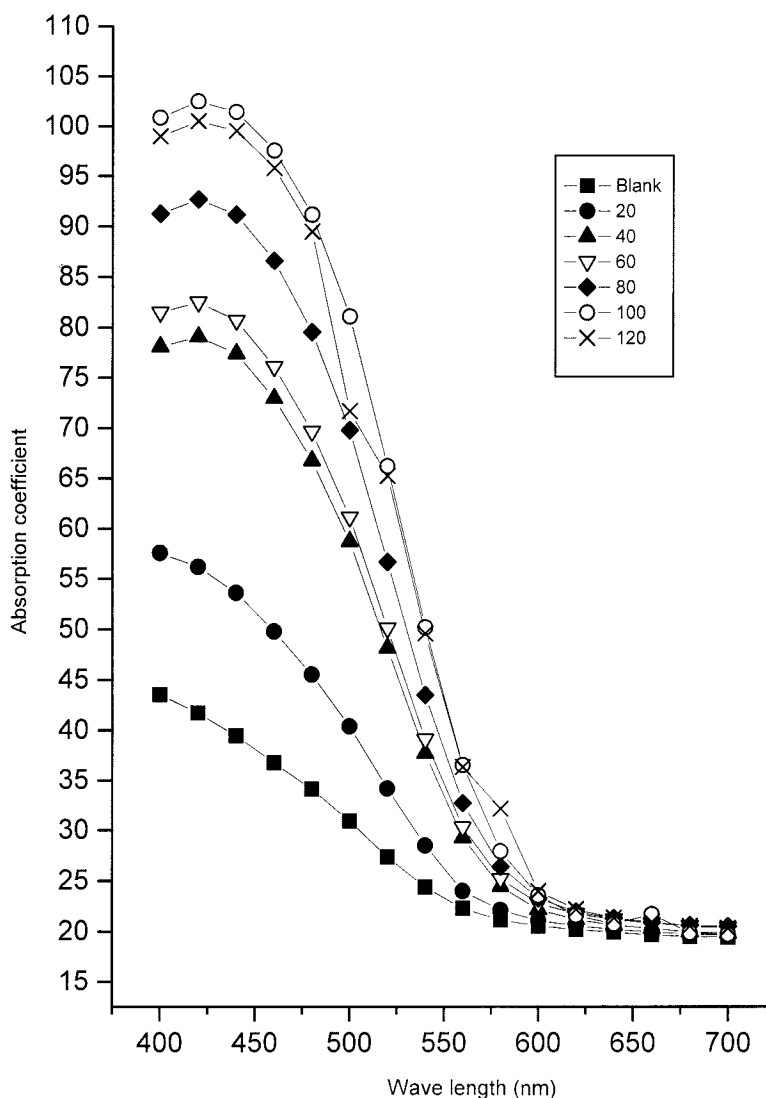


Figure 1 Effect of UV/ozone treatment for different times (minutes) on the α of wool fabrics dyed with the direct orange dye.

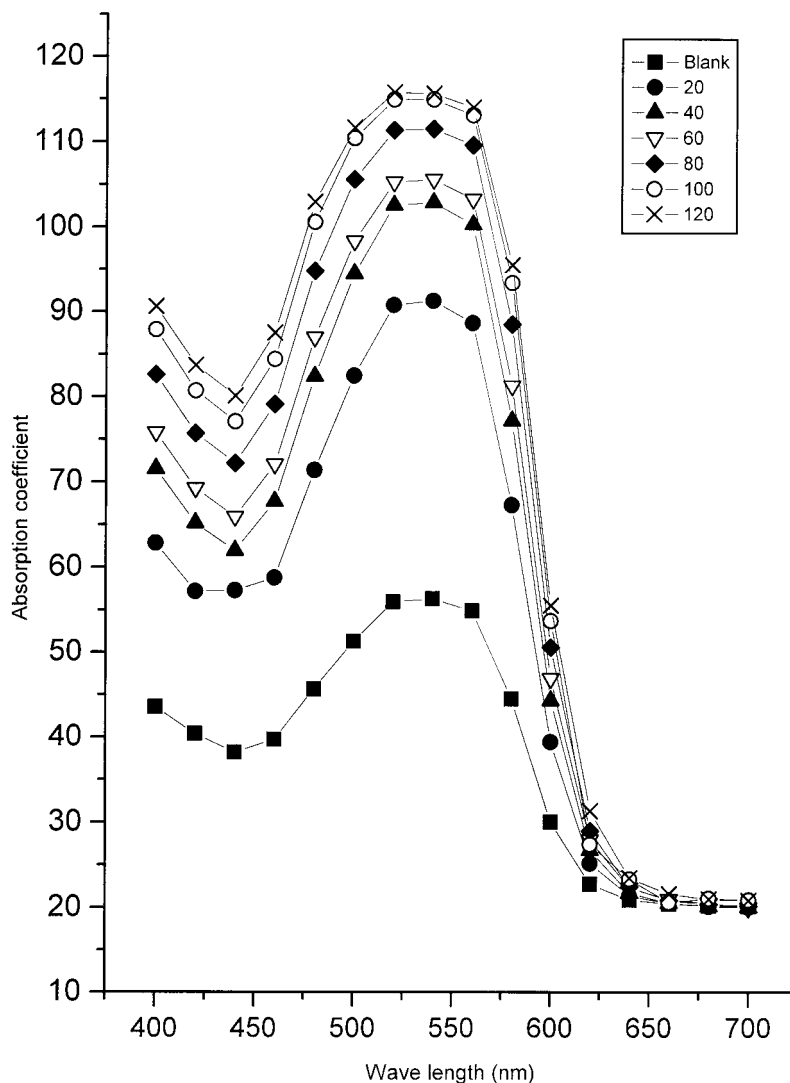


Figure 2 Effect of UV/ozone treatment for different times (minutes) on the α of wool fabrics dyed with the direct red dye.

Also, the α values for the reactive dye were higher than that of the direct dye.

Color parameters (L , a , and b)

To evaluate surface ΔE , a CIELAB^{25,26} system was used, where ΔE could be calculated from the following equation:

$$\Delta E = (\Delta L^2 + \Delta a^2 + \Delta b^2)^{1/2}$$

where $\Delta L = L_s - L_r$, $\Delta a = a_s - a_r$, and $\Delta b = b_s - b_r$, and s and r represent the sample and reference species, respectively. Tables II and III clarify the effect of UV/ozone treatments on the change in the color parameters. It was clear that L values decreased with increasing treatment times, that is, a darker color was obtained. Also, the treated samples dyed with the reactive dye gave a darker color than those dyed with

the direct dye. When the changes in the red–green component (a values), which are very sensitive to red dye under testing and changes in yellow–blue component (b values) for the direct dye were considered, generally, these values increased with increasing treatment times. These results agreed well with the k/s trend.

ΔE and LF characteristics

Figures 3 and 4 show the color difference ($\Delta E'$) values of the treated dyed samples before and after exposure to artificial daylight for about 150 h, whereas Tables II and III clarify the difference between them, that is, the changes that occurred due to exposure to artificial daylight, where

$$\Delta E' = \Delta E_{(\text{Treated dyed wool fabrics before exposure today light})} - \Delta E_{(\text{Treated dyed wool fabrics after exposure today light})}$$

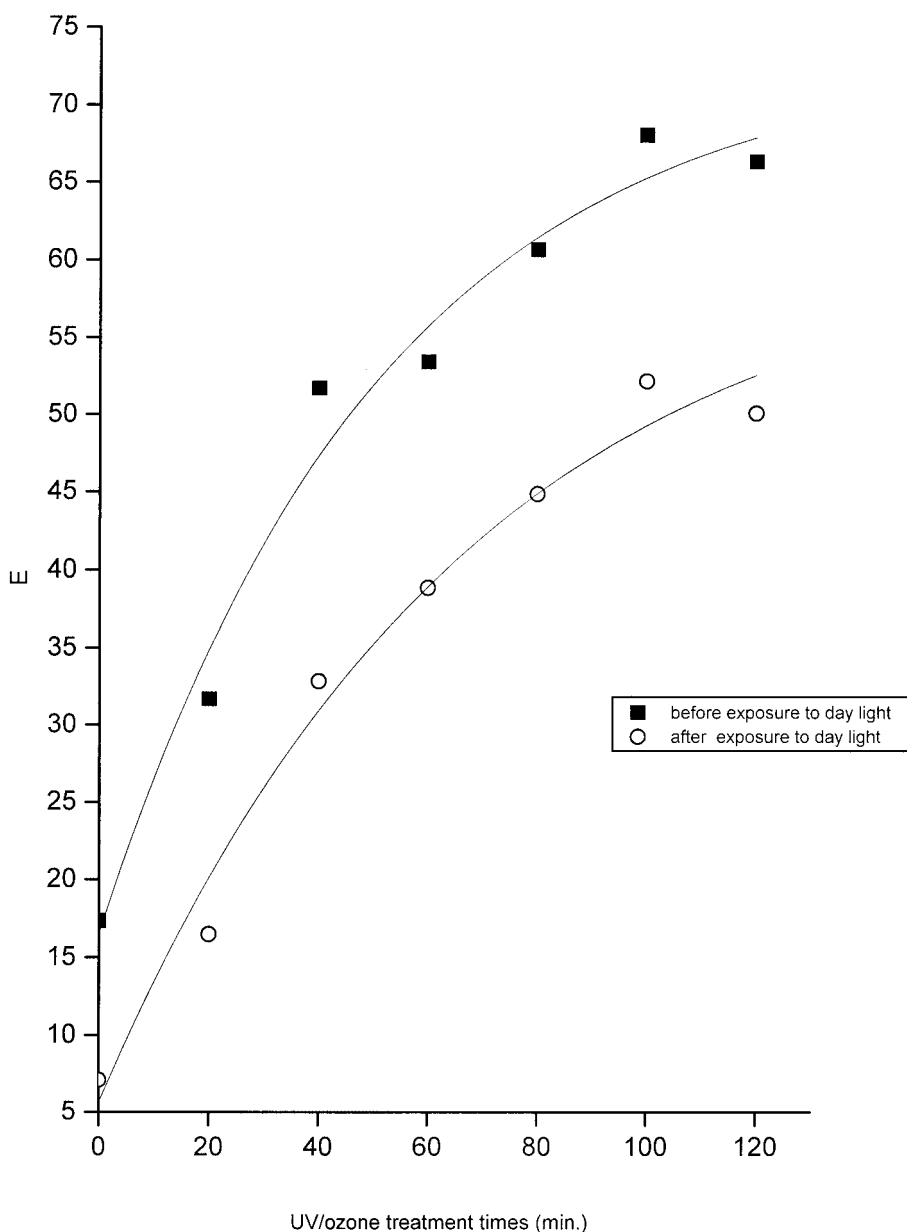


Figure 3 ΔE values at different UV/ozone treatment times for wool fabrics dyed with the direct orange dye before and after exposure to artificial daylight.

It was clear that with respect to the direct dye, there was no remarkable change in $\Delta E'$ with increasing treatment time, although the k/s values increased continuously. This means that with increasing treatment time, fading decreased; that is, the light fastness of the treated dyed samples that were exposed to artificial daylight increased as indicated in Tables II and III. This may have been due to increasing aggregation of dye particles inside the fiber pores, which lowered surface per weight²⁷ ratio of the treated dyed exposed fabrics.

When $\Delta E'$ for the reactive dye was considered, there were no changes before and after exposure to artificial daylight; that is, the two lines were coincident with

each other, as shown by the higher light fastness values (≈ 7) in Figure 4 and Table III. Thus, in addition to the effect of the UV/ozone treatment on the surface modification in the improvement of the dyeability and the increase in the aggregation of dye particles inside the fiber pores, it also strengthened the covalent bond formed between the reactive dye and thiol radicals due to the photooxidation of cystine.

CONCLUSION

The treatment of wool fabrics with UV/ozone significantly increased its wettability and permeability and reduced its weight loss; at the same time, the yellow-

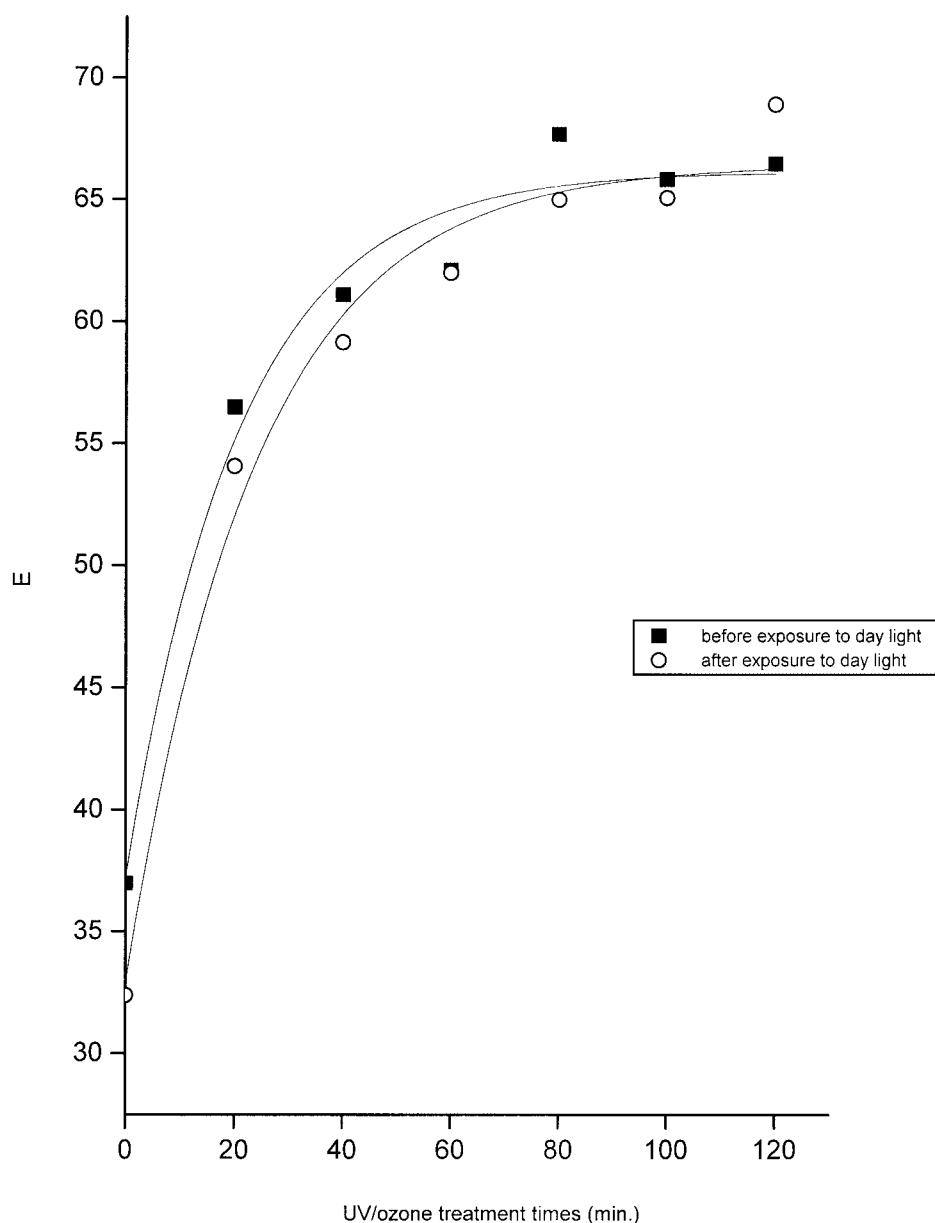


Figure 4 ΔE values at different UV/ozone treatment times for wool fabrics dyed with the direct red dye before and after exposure to artificial daylight.

ness index increased due to the analysis of photolabile amino acids to yield colored species on exposure to UV/ozone. These effects were more pronounced when the treatment was prolonged up to 100 h and were a possible consequence of the change in the surface of the cuticle scales of the wool fibers. The effects of this dry treatment on the improvement of the fabric properties were clarified through the study of the dyeing characteristics. The improvement in dyeability was more pronounced during the initial treatment times with a continuous increase with prolonged treatment up to 100 h. Also, the LF values were greatly improved. These results may have been due to the fact that the UV/ozone treatment activated the fiber sur-

face via the photooxidation of cystine linkage into a free-radical species, which promoted covalent bond formation between the fabrics and the dye. However, the treated wool samples could be dyed in a neutral media (pH \sim 7) at a lower temperature and a shorter time. Thus, UV/ozone treatment was of interest and showed several advantages in the aspects of energy savings, pollution control, and safety.

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