

# Time Optimization of Ultraviolet–Ozone Pretreatment for Improving Wool Fabrics Properties

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Received 31 August 2000; accepted 31 October 2001

**ABSTRACT:** Wool fabrics were exposed to ultraviolet (UV)–ozone treatment for different periods. After exposure, the fabrics were analyzed by Fourier transform infrared spectroscopy (FTIR). Also, the crystallinity and amorphousness regions were followed by an X-ray diffraction technique. The results were correlated by mechanical properties measurements. After a certain period of exposure, the dyeability and printability were improved because these abilities are strongly related to the percentage ratio of crystallinity regions to amorphousness regions in wool fabrics. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1469–1476, 2002

**Key words:** amorphous; crystallization; FTIR; X-ray; mechanical properties

## INTRODUCTION

Wool, natural keratin fibers (cutin fibrous protein), contains many kinds of cystine, thiocarbonic acid, and crosslinked polypeptide with a folding molecular structure. Wool is characterized by its relatively high nitrogen content, high ignition temperature, and high limiting oxygen index.<sup>1</sup> Wool is subject to much greater variability than its synthetic competitors, which can be controlled. Wool has a microstructure; that is, crystalline intermediate filaments surrounded by an amorphous matrix or so-called skin–core structure. In this structure, the inner cortex is hydrophilic because of the large number of polar groups contained in the polypeptide chains in the cortex. The outer surface of keratin fibers is water repellent, whereas the outer surface layer of cuticular cells (epicuticle) is hydrophobic<sup>2</sup> because this layer is thought to have a covalently bound lipid layer. This property accounts for the limited wet-

tability,<sup>3</sup> dyeability, and resistance to chemicals of wool.

The chemical reactivity of the disulfide bond in protein characterizes many of the properties of wool.<sup>4</sup> Furthermore it is the surface properties that are of particular significance in the pretreatment of wool fabrics and in determining their physical and chemical stability.

Wool is increasingly being used in blends with polyester, polyamide, and acrylic fabrics. The proportion of blends of wool with manmade fabrics is also constantly increasing.<sup>5</sup> Blends of polyester fibers with wool have acquired a special importance for their good dimensional stability and ease of care.

In this investigation, a new, AOX (adsorbable organic chlorides)-free pretreatment is suggested for improving dyeability, printability, and light fastness of wool fabrics. Optimization of the mechanical properties have also been considered.

Contamination of wastewater with AOX caused by chlorination<sup>6</sup> during the most widely used treatment for the wool dyeing process (chlorine /Hercosett) and the use of epichlorohydrine cause dangerous ecological problems. Because of the legal restrictions and the national and the

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*Journal of Applied Polymer Science*, Vol. 85, 1469–1476 (2002)  
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international awareness of ecology and pollution control, another AOX-free pretreatment is required to offer environmental advantages.

This recent pretreatment depends on exposing wool fabrics to ultraviolet (UV)-ozone for different periods of time. In UV-ozone treatment, the surface molecules of the wool fabrics are excited or dissociated by the absorption of short wavelength UV radiation in a photosensitized oxidation process. This process causes extensive surface modification at the outer epicuticle and exocuticle of wool fibers, and leads to the formation of cystic acid and free radicals species<sup>7</sup> and oxidation of disulfide bonds.

Also, it is supposed that photooxidation of the internal lipids is the initial step because they are obviously modified after a very short time of irradiation.

UV radiation at a wavelength of 184.9 nm is important because at this wavelength, oxygen is absorbed, which leads to the generation of ozone. Atomic oxygen is generated both when molecular oxygen is subjected to radiation at 184.9 nm radiation and when ozone is irradiated at 253.7 nm. Hydrocarbons and ozone absorb the 253.7 nm radiation and react with atomic oxygen to form simpler volatile molecules that disrobe from the surfaces. So, oxygen is generated and ozone is formed continuously and the latter is destroyed.

This method is suitable for wool fabric pretreatment and does not cause damage by heat to the fabrics because the modification is carried out under mild thermal conditions (or low temperatures). Thus, beneficial improvements to wool dyeability, printability, and shrink resistance properties<sup>8</sup> may be achieved.

## EXPERIMENTAL

### Material and UV-Ozone Treatment

Egyptian pure untreated wool fabrics (137 g/cm<sup>2</sup>) were supplied by Goldentex Company, Egypt. Strip wool samples of the area required for each test were mounted between two rings of circular-shaped metal diaphragms of 20-cm diameter. The samples were exposed in a closed box of dimensions 60 × 60 × 60 cm<sup>3</sup> to a bare burner of a UV lamp, after breaking its outer glass envelope (LRF 02971,400 W, 220 V, made in Poland). The lamp burner was fixed at the center of the diaphragms to obtain uniform and vertical exposure.

### Fourier Transform Infrared Analysis

Fourier transform infrared (FTIR) spectra were recorded for wool fabrics with a Perkin Elmer FTIR spectrophotometer (model 1650). The changes in some chemical groups contents were monitored with transmitted IR radiation at selected bands. Second derivative absorbance spectra were obtained with an FTIR Unit Bruker-Vector 22.

The optical density of these spectra were calculated and plotted according to the relation<sup>9</sup>

$$\text{optical density} \propto \log 1/T \quad (1)$$

where  $T\%$  is the transmittance value of the samples.

### X-ray Diffraction Technique

A Scintag Inc. diffractometer with CuK radiation was operated at 45 kV, 40 mA, and a wavelength  $\lambda = 1540.6 \text{ \AA}$ . The diffractograms were recorded in the range  $2\theta = 5\text{--}50^\circ$  continuous at scan rate of  $2^\circ/\text{min}$ .

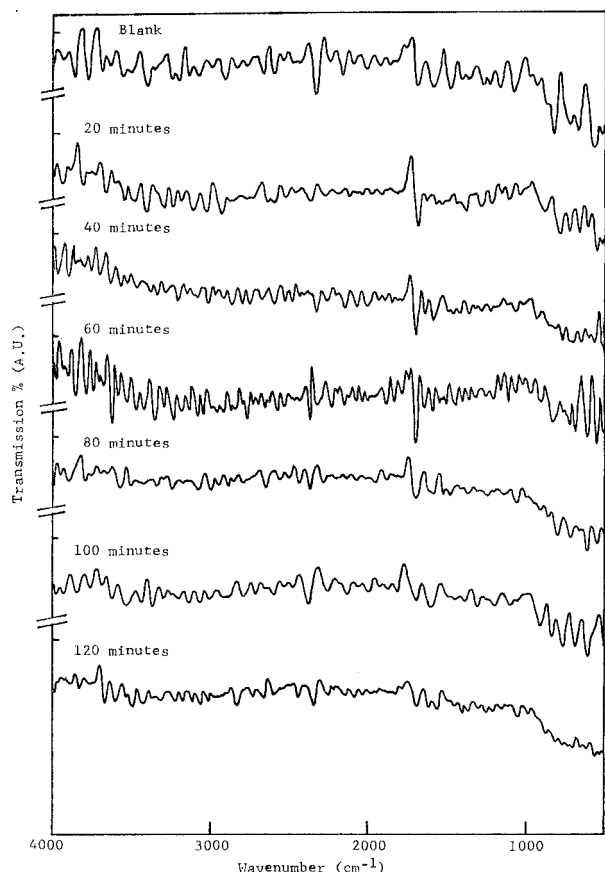
The relation of Segal et al.<sup>10</sup> was used to compute the crystallinity index (Cr.I) for wool:

$$\text{Cr.I} = (I_f - I_s)/I_f \times 100 \quad (2)$$

where  $I_f$  is the peak intensity of the fundamental band  $2\theta = 12\text{--}13^\circ$ , and  $I_s$  is the peak intensity of the secondary band  $2\theta = 25\text{--}25.5^\circ$ .

### Mechanical Properties Measurements

Untreated wool samples and wool samples treated with UV-ozone were tested for tensile strength and elongation percentage at break. The samples in strip form (5 cm wide and 20 cm long) were tested with a Shimadzu Universal tester type S-500 (C.R.T., Japan), keeping a gauge length of 10 cm and cross-head speed of 10 cm/min, by a universal method of testing [ASTM Book of Standards, D1455-64T, 325-332, 1964, B.S. Handbook Methods of Test for Textiles, 1956]. An average of 10 readings was made for each measurement. Each of the strength and the percentage elongation measurements was corrected by using a standard international value and a particular test sample. The efficiency of correction is equal to ratio between the standard international value and a test value for comparison.



**Figure 1** Changes in the shape and transmittance intensity of the infrared chemical groups of wool fabric in response to various UV-ozone exposure times.

**RESULTS AND DISCUSSION**

**FTIR Spectroscopy**

The FTIR transmittance spectra of all wool samples after different treatment times are presented in Figure 1 as function of wave number in the range 500–4000 cm<sup>-1</sup>. Exposed and unexposed wool samples were analyzed by considering some chemical groups using FTIR spectroscopy. These groups are presented in Table I. The peaks at certain wavelengths shown in Table I are taken to represent the groups band intensities for different exposure times and are represented in Figure 2, whereas the second derivatives of the absorbance spectra of the same samples are presented in Figure 3.

For group C=O at 1699.5 cm<sup>-1</sup>, the intensity drops drastically to ~60% of its initial value after 60 min of exposure, then increases to near its initial value after 80 min, and then decreases in

**Table I** Chemical Groups Transmission Intensities after Different Times of Exposure

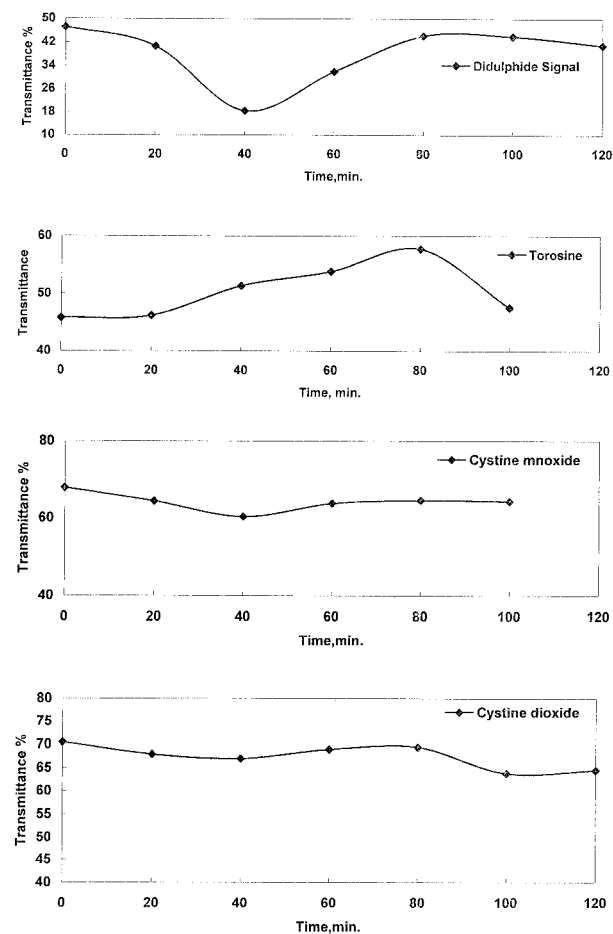
Time, min	Disulfide Single		Tyrosine		Cystine Monoxide		Cystine Dioxide		O-H First Overtone		C=O Group		C-H str Band (2900)		O-H		
	500-590 cm <sup>-1</sup>	840-896 cm <sup>-1</sup>	1070-1120 cm <sup>-1</sup>	1120-1200 cm <sup>-1</sup>	1540-1600 cm <sup>-1</sup>	1699.5 cm <sup>-1</sup>	2750-3000 cm <sup>-1</sup>	3370-3450 cm <sup>-1</sup>	70.84	71.01	74.90	72.21	56.35	69.81	60.69	66.16	67.64
0	47.27	45.85	67.83	70.50	70.84	71.01	74.90	72.21	70.84	71.01	74.90	72.21	56.35	69.81	60.69	66.16	67.64
20	40.68	46.22	64.42	67.92	64.19	49.60	57.33	56.35	64.19	49.60	57.33	56.35	56.35	69.81	60.69	66.16	67.64
40	18.46	51.36	60.35	—	56.83	48.45	66.86	69.81	56.83	48.45	66.86	69.81	66.86	69.81	60.69	66.16	67.64
60	31.92	53.88	63.82	68.92	59.54	42.31	59.14	60.69	59.54	42.31	59.14	60.69	59.14	60.69	60.69	66.16	67.64
80	44.18	57.78	64.58	69.40	69.87	67.96	74.71	66.16	69.87	67.96	74.71	66.16	66.16	60.69	60.69	66.16	67.64
100	44.00	47.59	64.33	63.77	63.30	65.70	68.33	66.16	63.30	65.70	68.33	66.16	66.16	60.69	60.69	66.16	67.64
120	40.91	—	—	64.44	64.83	65.58	69.72	67.64	64.83	65.58	69.72	67.64	67.64	60.69	60.69	66.16	67.64

an unremarkable manner until 120 min of exposure. With respect to group O—H st. first overtone 1540+50, the same trend was noticed, but the main drop in intensity (20%) occurs after 40 min, then it increases to above its initial value at 80 min of exposure, and then it decreases slowly until 120 min.

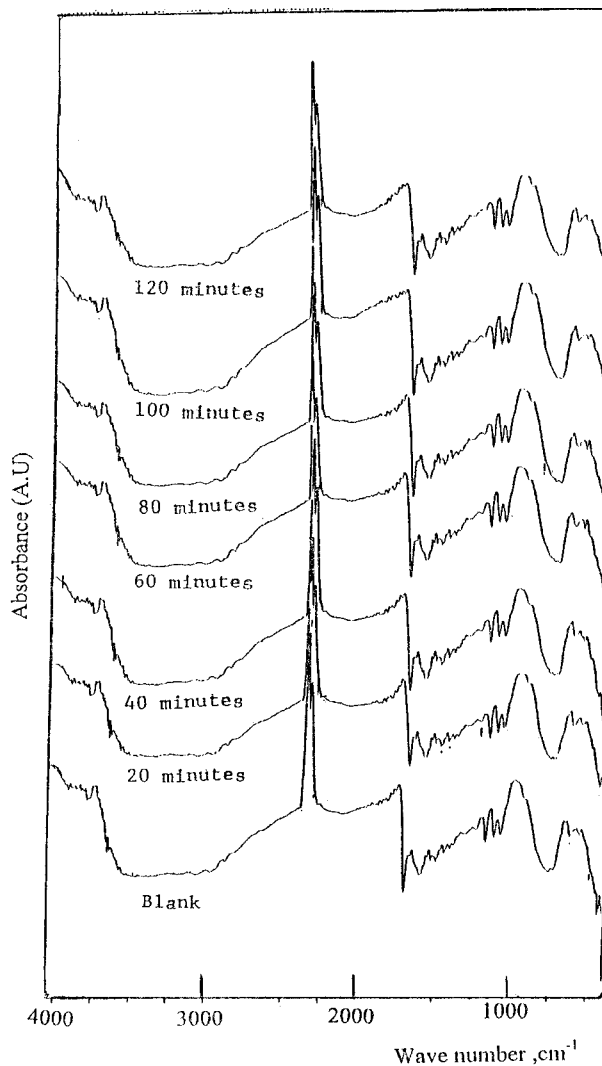
The group at 1090+30  $\text{cm}^{-1}$ , which represents cystine oxides, follows the same pattern of increase and decrease in intensity as the group at 1540+50, but by a small percentage and the last group disappears after 120 min of exposure.

For the group at 854  $\text{cm}^{-1}$ , which indicates tyrosine, the intensity increases gradually by ~26% of that of the unexposed samples after 80 min of exposure, then decreases after 100 min, and then completely disappears after 120 min.

The relation between optical density as a function of exposure time for the same chemical



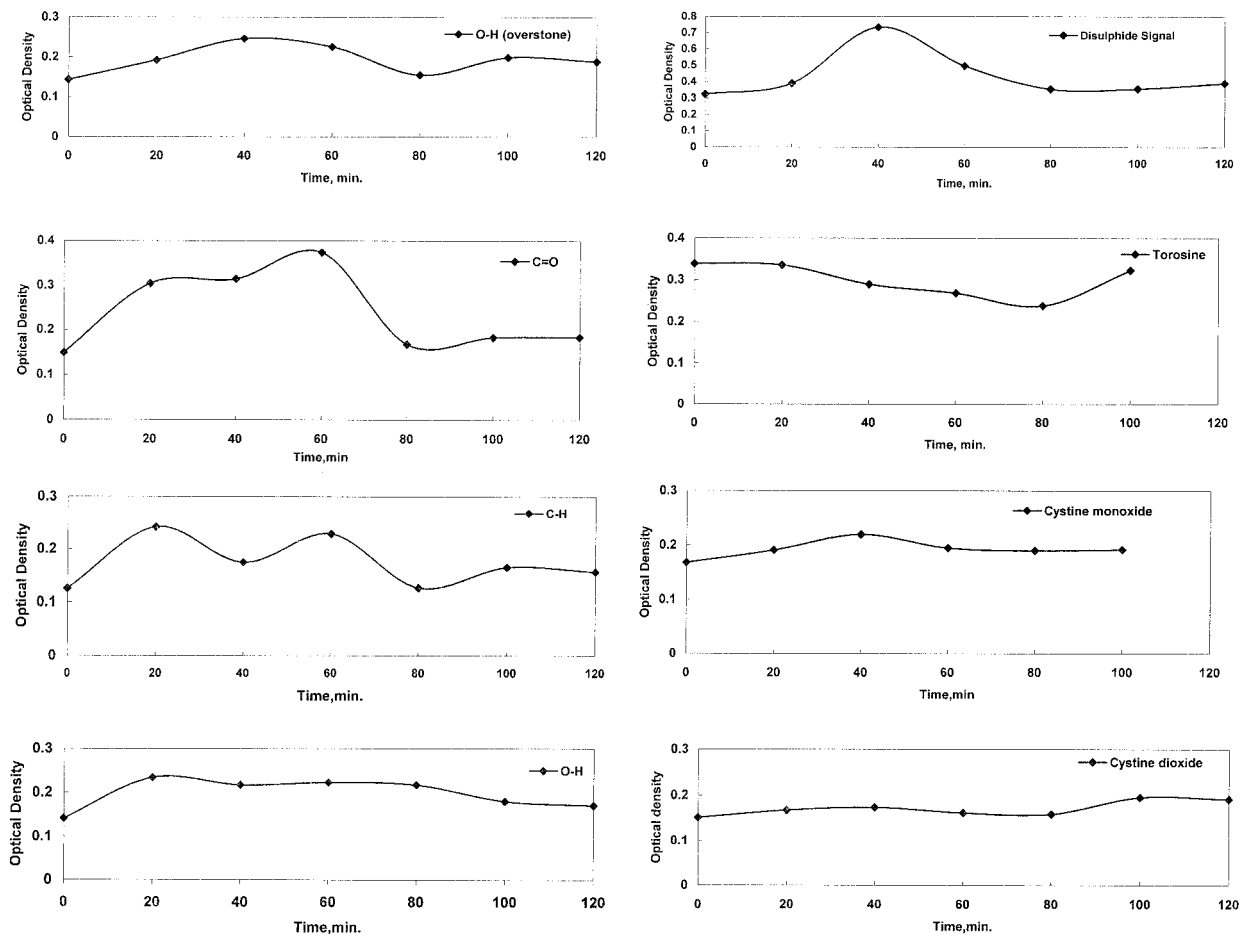
**Figure 2** Group band intensity of eight chemical groups of wool fabrics in relationship to UV-ozone exposure times.



**Figure 3** The second derivatives of the absorbance spectra of the wool fabrics in relationship to UV-ozone exposure times.

groups for all samples under investigation is shown in Figure 4. It is clear from the figure that there is an increase in the optical density of the wool chemical groups C—H st., C=O after 60 min of exposure then a drop occur after 100 and 120 min.

For group O—H st. first overtone, cystine monoxide and disulfide signal, the optical density reaches a maximum after 40 min of exposure, then a drop occurs after 60 min. This drop is followed by an increase with respect to the first group (O—H st.) and no change for the second group (cystine monoxide) until 120 min of exposure. In contrast, the disulfide signal continues to decrease in optical density until 80 min, stays



**Figure 4** The relation between optical density of the chemical groups of wool fabrics and UV-ozone exposure times.

nearly unchanged after 100 min, and then increases slightly after 120 min of exposure.

The increase in optical density of these chemical groups represents an increase in Irabsorption, which indicates a change in the molecular configuration of wool. It is noted that wool fabrics took on a pale greenish color after long treatment. This color gradually changed to yellow on standing. Cystyl radicals may be the cause of this greenish color.<sup>4</sup>

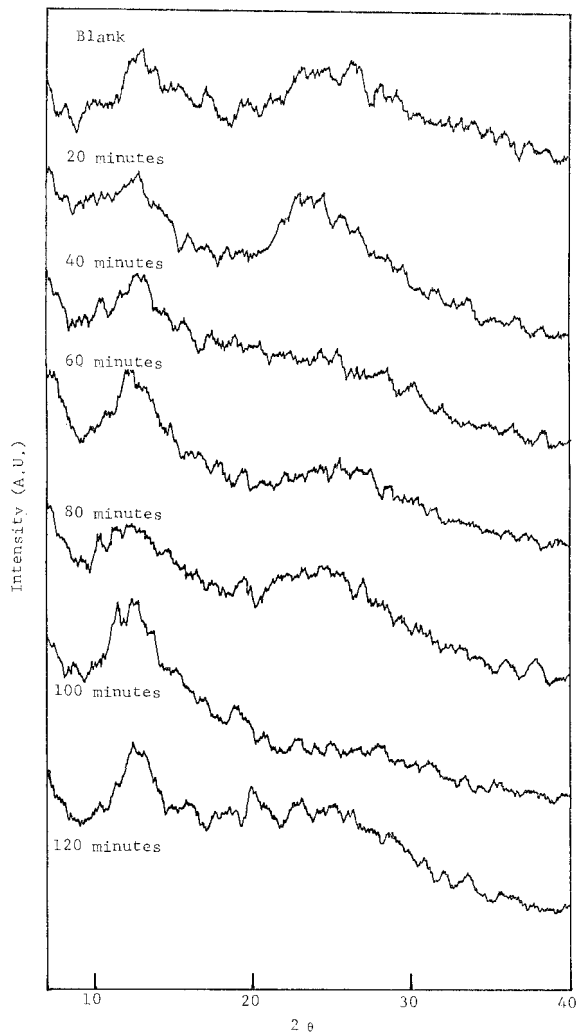
### X-ray Diffraction Technique

The X-ray diffraction patterns for wool samples unexposed and exposed to UV-ozone after different periods are shown in Figure 5. Band intensities for the peaks are represented in Figure 6. Two distinguished bands are centered at ( $2\theta = 12-13$ ) and  $2\theta = 25-25.5$ . It is noticed from the patterns that a new band starts to appear at  $2\theta = 18-20$  after 60 min of exposure. The intensity

of these bands are also shown in Figure 6. By following the first band intensity ( $2\theta = 12-13$ ), it is noticed that it stays nearly constant until 60 min of exposure, then decreases by a small value of 7.6% of its normal value after 80 min of exposure, and then increases by  $\sim 13\%$  of its normal value after 100 min; unremarkable changes occurred after 120 min of exposure.

The second band at  $2\theta = 25-25.5$  starts high in intensity then continues decreasing until it reaches a minimum value ( $\sim 70\%$  of its normal value) after 60 min of exposure. An increase then decrease then increase again to nearly the same value after 80, 100, and 120 min of exposure, respectively, is shown for this band.

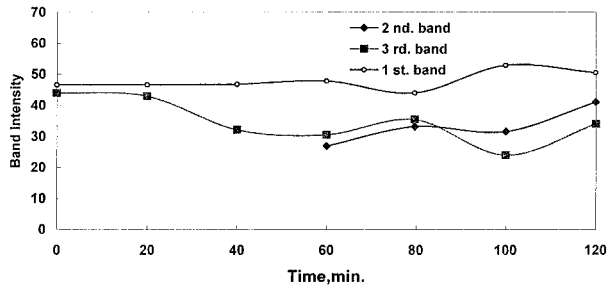
The third band ( $2\theta = 18-20$ ), which starts to appear after 60 min of UV-ozone exposure, follows the same pattern as the second band intensity but with different values of change.



**Figure 5** X-ray diffraction patterns for wool fabrics at different UV-ozone exposure times.

These results suggest that there is a significant structural change in the wool fabrics due to the induced effect of the UV-ozone exposure. This exposure produced variation in the crystallinity/amorphousity ratio because a higher intensity indicates growth of the crystalline regions, whereas a lower intensity indicates the tendency of the wool samples to be amorphous. By modifying this ratio so that the amorphousity region dominates, improvement in dyeability and printability properties can be achieved. Mechanical deterioration must be avoided at the same time, so an optimizing time for UV-ozone treatment must be determined to accomplish these two goals of improving dyeability and printability without mechanical deterioration.

The half-band width of the X-ray patterns versus exposure time for the first band only ( $2\theta = 12-$



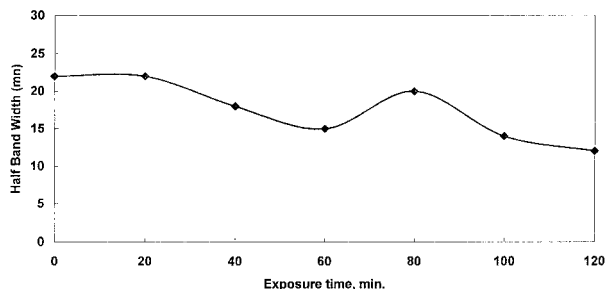
**Figure 6** Band intensity of X-ray diffraction patterns for wool fabrics after different time of exposure to UV-ozone treatment.

13) are shown in Figure 7. It is evident from the figure that the half width of this band decreased continuously during exposure until 60 min, which means that the crystallite size became larger<sup>11, 12</sup>(inverse relation). After 80 min of exposure, the half-band width increases (crystallite size decreases) and returns to nearly its normal value and then decreases after 100 and 120 min of exposure (increase in crystallite size).

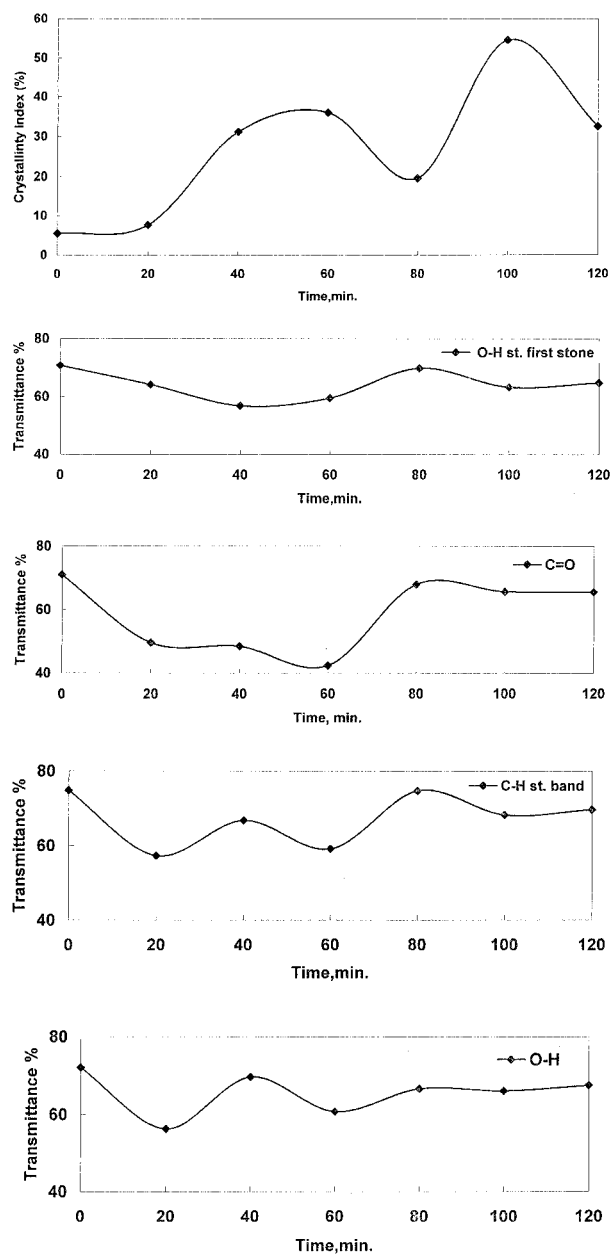
The crystallinity index values Figure 8 indicate that the lowest value occurs after 80 min of exposure (amorphousity increases). Crystalline regions inside the polymer are irreversibly transformed into amorphous ones<sup>11</sup> on exposure to ionizing radiation. This behavior implies destruction of the structural regularity of the main chains of the polymeric molecules on exposure to ionizing radiation. After 100 min, the crystallinity index increases again and then decrease during 120 min of exposure, but does reach to its values at 80 min of exposure.

**Mechanical Properties Measurements**

Changes in tensile strength, elongation percentage, and Young's modulus of wool samples after

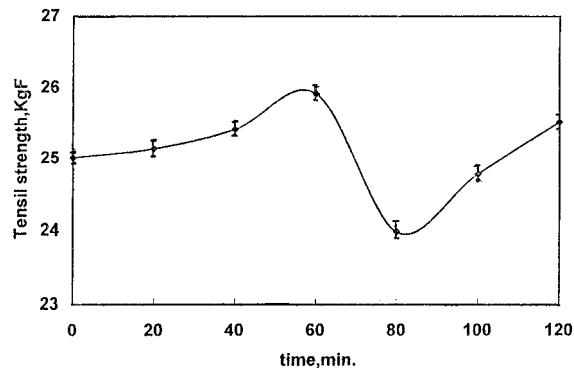


**Figure 7** Relation between half bandwidth of X-ray patterns for the first band for wool fabrics treated at different times by UV-ozone.



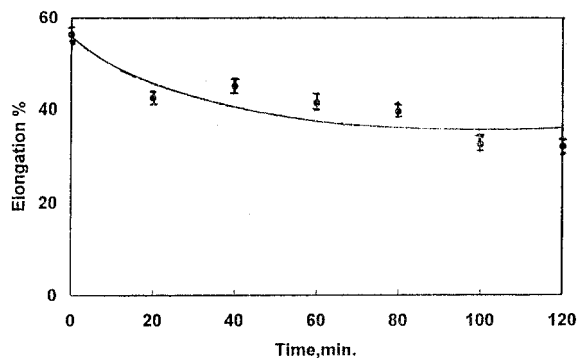
**Figure 8** Relation between crystallinity index (%) of wool fabrics and UV-ozone exposure times.

various UV-ozone exposure times are shown in Figures 9, 10, and 11, respectively. Tensile strength increases in value slightly, whereas samples experience less elongation until ~60 min of exposure. This result may be due to the dominance of crosslinking reactions over chain scission during these stages<sup>13</sup> and the increasing amount of crosslinked macromolecules. After 80 min of exposure, samples break more easily and the strength drops by a value of ~4% of its normal

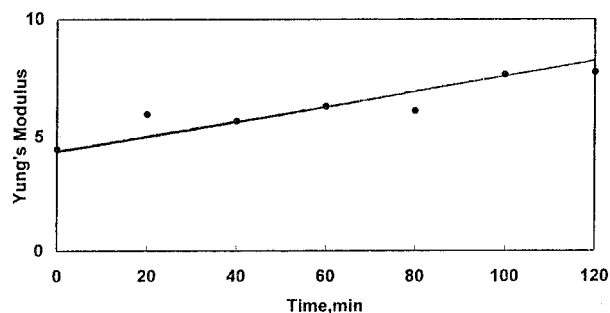


**Figure 9** Variation of tensile strength as a function of UV-ozone exposure times for wool fabrics.

value. This break down, combining with FTIR analysis is attributed to a decrease in the average molecular length by the scission of the polymer chains.<sup>14, 15</sup> Also, this break indicates that the bulk properties of wool are affected, which is reflected in the mechanical strength. After 80 min of exposure, the elongation percentage continues decreasing. Elongation seems to be the physical property most sensitive to the photolytic processes. Photochemical processes initiate reactions like chains cleavage, crosslinking, and preoxidation or elimination of small molecules. These reactions lead to changed physical and chemical properties of fabrics and may reveal facial formation of wool protein crosslinks.<sup>16</sup> Many scientists correlated the alternation of tensile strength with chemical changes in proteins.<sup>17-21</sup> The main reason for changing fabrics strength was assumed to be the cleavage or crosslink of the cystine bridges<sup>18</sup> or of the main chain bonds between  $\alpha$ -C atom and the amide-N atom of the wool proteins.<sup>21</sup>



**Figure 10** Variation of elongation as a function of UV-ozone exposure times for wool fabrics.



**Figure 11** Relation between Young's modulus values for exposure of wool fabric to UV-ozone for different times.

Weatheral<sup>21</sup> detected chemical evidence for breakdown of protein chains with the formation of primary amide and carbonyl groups, which causes loss in bursting strength and abrasion resistance of wool fabrics. As a result of chain scission, the chains become shorter and a new orientation for regular alignment is achieved. The crystallinity increases as a result of closer packing of the chains. Roper and Finnimore<sup>19</sup> found spectroscopic evidence of irradiation-induced decrease of the cystine content and, at the same time, decreasing wet bundle strength. Alexander and Hudson<sup>22</sup> reported that both tensile strength and elongation of wool fabrics reflect the integrity of the main protein because the strength is sensitive to peptide scission. Also, there is a linear relationship between the loss of strength of heated wool yarns and the amount of protein scission measured in terms of ketoacyl end groups formed.<sup>17</sup>

So the decrease in elongation percentage values and also in elasticity could be attributed to the difference in the amorphous region and the nature of the crystalline region because there is an increase in crystallinity perfection and growth of new lamellae in the amorphous region.

## CONCLUSION

UV-ozone pretreatment of wool fabrics has been proven to increase dyeability and printability properties after ~80 min of exposure because after this time, the amorphous region dominates over the crystalline one. Also after this time, no significant deterioration (4%) in the mechanical properties of the wool fabrics was observed. Therefore, the UV-ozone pretreatment after a certain optimizing time may be the best alternative process to the conventional chlorination

method because there is no waste water produced. Also, the sulfurous smell, which occurs after exposure, disappears after some days.

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