# Chemical Modification of Nylon 6 and Polyester Fabrics by Ozone-Gas Treatment

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**ABSTRACT:** In a previous article, we reported on the ozone-gas treatment of wool and silk fabrics in relation to the gas-phase processing of textile fabrics. The treatment incorporated an oxygen element into the fiber surface and contributed to an increase in water penetration into the fabric. In this study, nylon 6 and polyester fabrics were treated with ozone gas in the same way as that of the wool and silk fabrics. The treatment incorporated much more oxygen into the fiber surface in the form of —COH and —COOH, as shown by electron spectroscopy for chemical analysis. Water penetration increased considerably with treatment, and the apparent dyeing rate and equilibrium dye uptake were also improved, especially for the polyester fabric, despite an increase in the crystallinity. Therefore, it seemed that the treatment brought about a change not only in the fiber surface but also in the internal structure of the fibers (the crystalline and amorphous regions) with regard to the dyeing behavior. Further, the mechanical characteristics of the ozone-gas-treated polyester and nylon 6 fabrics were measured with a Kawabata evaluation system apparatus. The shearing modulus and hysteresis widths increased with treatment, especially for the polyester fabric. Therefore, it was clear that the treatment caused a change in the fabric hand to crisp.  J Appl Polym Sci 100: 1344–1348, 2006

**Key words:** dyes/pigments; ESCA/XPS; mechanical properties; nylon; polyesters

## INTRODUCTION

Previously, cellulosic, wool, and silk fabrics have been treated with ammonia gas in gas-phase processing of textile finishing.[1–4] It is known that ozone is an excellent oxidizing agent. The treatment has been of interest in textile finishing from the standpoint of environmental preservation.[5–8] Ozone bleaching of cotton fabric and ozone shrink-resistant finishing of wool fabric have been investigated.[2,4] Recently, we studied the ozone-gas treatment of textile fabrics. In a previous article, wool and silk fabrics were processed with ozone gas.[8] To measure surface modification, electron spectroscopy for chemical analysis (ESCA) was carried out. The $O_{1s}$ intensity increased, especially for wool. As shown by the curve fitting of the $C_{1s}$ spectra, oxygen was incorporated in the form of —OH and —COOH on the fiber surface. As the result, the wettability was remarkably improved. Also, the apparent dyeing rate and equilibrium dye uptake increased apparently, and the shrink resistance of the silk fabric was controlled considerably by the treatment. Therefore, it seemed that the treatment caused a change not only in the fiber surface but also in the internal structure, such as in the crystalline and amorphous regions of the fibers.

In this study, nylon 6 and polyester fabrics were treated with ozone gas with various treatment conditions. The results were evaluated on the basis of ESCA surface analysis, crystallinity, water penetration, and dyeing properties. In addition, the mechanical properties of the nylon 6 and polyester fabrics processed with ozone gas were measured with a Kawabata evaluation system (KES) apparatus. The shearing parameters evaluated were shearing modulus ($G$) and hysteresis widths ($2HG$ and $2HG5$). The effects of treatment on the mechanical properties of the fabrics were evaluated on the basis of these parameters.

## EXPERIMENTAL

### Materials and treatment

Polyester taffeta (57 g/m$^2$) and nylon 6 taffeta (58 g/m$^2$) fabrics were used as materials. Ozone-gas treatment was carried out with the equipment shown in Figure 1[8] for 10 min at atmospheric pressure (AP) and at 0.1 MPa.

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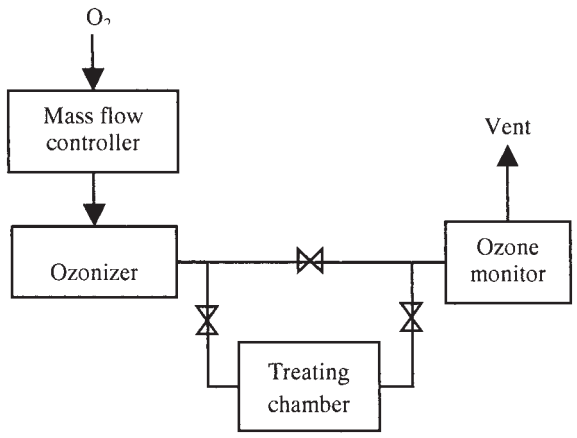



**Figure 1** Flow chart for ozone-gas treatment.

## Measurements

To investigate the surface chemical constitution of the fibers by ozone-gas treatment, ESCA was carried out with a VG Scientific ESCALAB 250 spectrometer (West Sussex, UK). From the wide-scanning ESCA spectra, the relative intensities of the $C_{1s}$, $O_{1s}$, and $N_{1s}$ spectra were measured. Furthermore, to elucidate the details of the chemical composition, curve fitting of the $C_{1s}$ spectra was performed, and the relative components of —CH, —COH, and —COOH were determined.

Moisture regain and water absorption were measured by the following method.[8] The treated fabric was immersed in water for 24 h, centrifuged for 20 min at 3000 rpm ($W_1$), kept for 48 h at 65% relative humidity ($W_2$), and finally dried for 3 h at 105°C ($W_0$). Moisture regain and water absorption were calculated by the following equations:[8]

$$\text{Moisture regain (\%)} = \frac{W_2 - W_0}{W_0} \times 100$$

**TABLE I**
**Relative Intensities of $C_{1s}$, $O_{1s}$, and $N_{1s}$ in Wide-Scanning ESC Analysis of Nylon 6 and Polyester Fabrics Treated with Ozone Gas**

| Treatment | Surface chemical composition (%) | | |
|---|---|---|---|
| | $C_{1s}$ | $O_{1s}$ | $N_{1s}$ |
| Nylon 6 fabric | | | |
| Untreated | 83.5 | 12.7 | 3.8 |
| Ozone-gas treated | | | |
| AP, 20°C/10 min | 79.8 | 15.5 | 4.7 |
| Polyester fabric | | | |
| Untreated | 75.2 | 24.8 | — |
| Ozone-gas treated | | | |
| AP, 20°C/10 min | 74.8 | 25.2 | — |
| 0.1 MPa, 20°C/10 min | 74.2 | 25.8 | — |

**TABLE II**
**Wave Separation of $C_{1s}$ Spectra of Nylon 6 and Polyester Fabrics Treated with Ozone Gas**

| Treatment | Relative peak area (%) | | |
|---|---|---|---|
| | —CH | —COH | —COOH |
| Nylon 6 fabric | | | |
| Untreated | 49.2 | 39.5 | 11.3 |
| Ozone-gas treated | | | |
| AP, 20°C/10 min | 44.0 | 38.1 | 17.9 |
| Polyester fabric | | | |
| Untreated | 73.2 | 12.2 | 14.6 |
| Ozone-gas treated | | | |
| AP, 20°C/10 min | 71.6 | 14.4 | 14.0 |
| 0.1 MPa, 20°C/10 min | 59.5 | 20.8 | 19.6 |

$$\text{Water absorption (\%)} = \frac{W_1 - W_0}{W_0} \times 100$$

Water penetration was obtained by the time of disappearance of 0.1 mL of water on the fabric. The density of the treated fabrics was measured at 23°C with the $CCl_4$/*n*-heptane density gradient column method, and the weight fraction crystallinity ($X_c$) was calculated by the following equation for the polyester fiber:

$$X_c(\%) = \frac{\rho_c(\rho - \rho_a)}{\rho(\rho_c - \rho_a)} \times 100$$

where $\rho$ is the measured density of the samples, $\rho_c$ is the density of the crystallite of the polyester (1.455 g/cm$^3$) and $\rho_a$ is the density of amorphous region of the polyester (1.335 g/cm$^3$). On the other hand, the nylon 6 fiber coexisted in $\alpha$ and $\gamma$ forms, which had different densities. Therefore, it was difficult to obtain the crystallinity by the density gradient column method. Therefore, the density obtained by the den-

**TABLE III**
**Effect of Ozone-Gas Treatment on Water Penetration, Moisture Regain, and Water Absorption of Nylon 6 and Polyester Fabrics**

| Treatment | Time of water penetration (s) | Moisture regain (%) | Water absorption (%) |
|---|---|---|---|
| Nylon 6 fabric | | | |
| Untreated | 493 | 3.65 | 6.08 |
| Ozone-gas treated | | | |
| AP, 20°C/10 min | 105 | 3.72 | 6.10 |
| Polyester fabric | | | |
| Untreated | 300 | 0.22 | 0.22 |
| Ozone-gas treated | | | |
| AP, 20°C/10 min | 127 | 0.28 | 0.54 |
| 0.1 MPa, 20°C/10 min | 66 | 0.28 | 0.69 |

**TABLE IV**
**Crystallinity of Ozone-Gas Treated Nylon 6 and Polyester Fabrics as Measured by the Density Gradient Column Method**

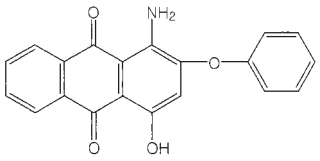
| Treatment | Crystallinity (%) | Density ($g/cm^3$) |
|---|---|---|
| Nylon 6 fabric | | |
| Untreated | | 1.144 |
| Ozone-gas treated | | |
| AP, 20°C/10 min | | 1.153 |
| Polyester fabric | | |
| Untreated | 52.2 | |
| Ozone-gas treated | | |
| AP, 20°C/10 min | 53.0 | |
| 0.1 MPa, 20°C/10 min | 54.7 | |

sity gradient column method was indicated as a measure of the crystallinity for the nylon 6 fiber. As a measure of the mechanical properties of the fabric, a shearing hysteresis curve was measured with a KES (F-7 Kato Tech, Japan)[9] and *G*, 2*HG*, and 2*HG*5 were obtained.

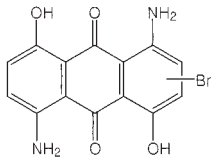
### Dyeing

The ozone-gas-treated fabrics were dyed with the commercial disperse dyes Red 60 and Blue 56:

Disperse Red 60




Disperse Blue 56




Dyeing was done at a concentration of $2 \times 10^{-3}$ mol/L at 100°C, and the equilibrium dye uptake was obtained after dyeing for 120 h at 100°C. The fabric was extracted with 100% dimethylformamide, and dye uptake was determined photometrically.

## RESULTS AND DISCUSSION

### ESCA

In a previous article,[3] we reported that the ozone-gas treatment of wool and silk fabrics increased the $O_{1s}$ intensity and accelerated the water penetration into the fabric. Table I shows the relative intensities of the $C_{1s}$, $O_{1s}$, and $N_{1s}$ spectra in the wide-scanning ESCA of the ozone-gas-treated nylon 6 and polyester fabrics. As shown in Table I, the $O_{1s}$ intensity of the nylon 6 fabric increased apparently by AP, whereas the intensity of the polyester fabric increased with increasing gas pressure. To elucidate the details of oxygen on the fiber surface, curve fitting of the $C_{1s}$ spectra for the fabrics was done, and the —COH and —COOH peaks at 286.5 and 288.5 eV are summarized in Table II. The —COH and —COOH contents were increased considerably by the treatment. From the results, it is clear that polymer surfaces of the polyester and nylon 6 fibers were easily oxidized by the ozone-gas treatment. Although the intensity of the polyester fabric did not change under atmospheric conditions, each peak area increased considerably with increasing gas pressure.

### Water penetration, water absorption, and crystallinity

We expected that an increase in the $O_{1s}$ intensity of ozone-gas-treated fabrics would lead to an improve-

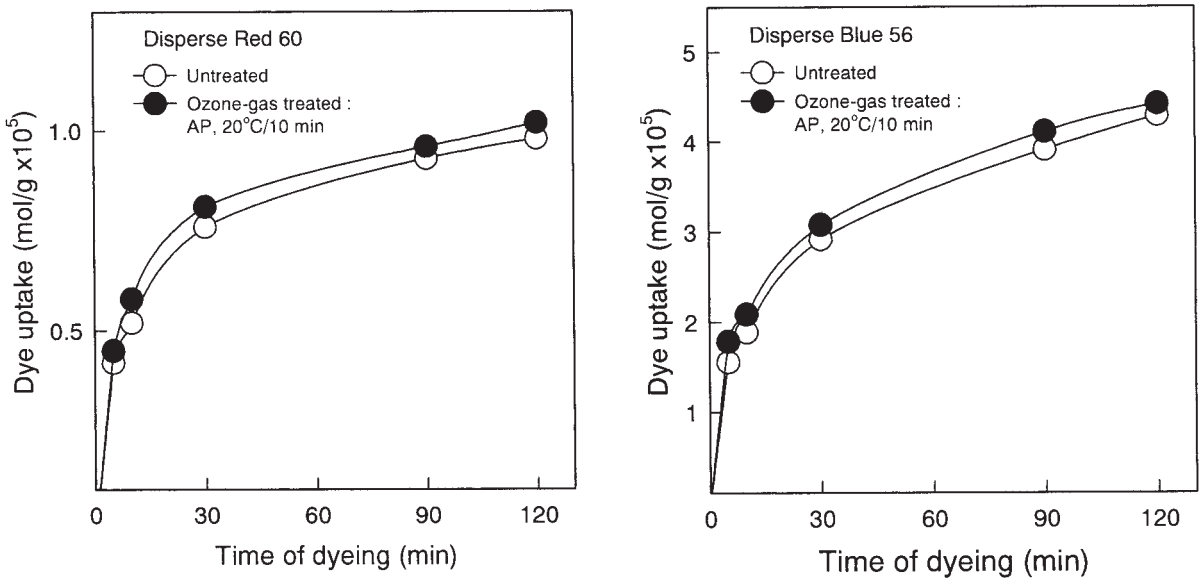



**Figure 2** Dyeing rates of disperse dyes on ozone-gas-treated nylon 6 fabric.

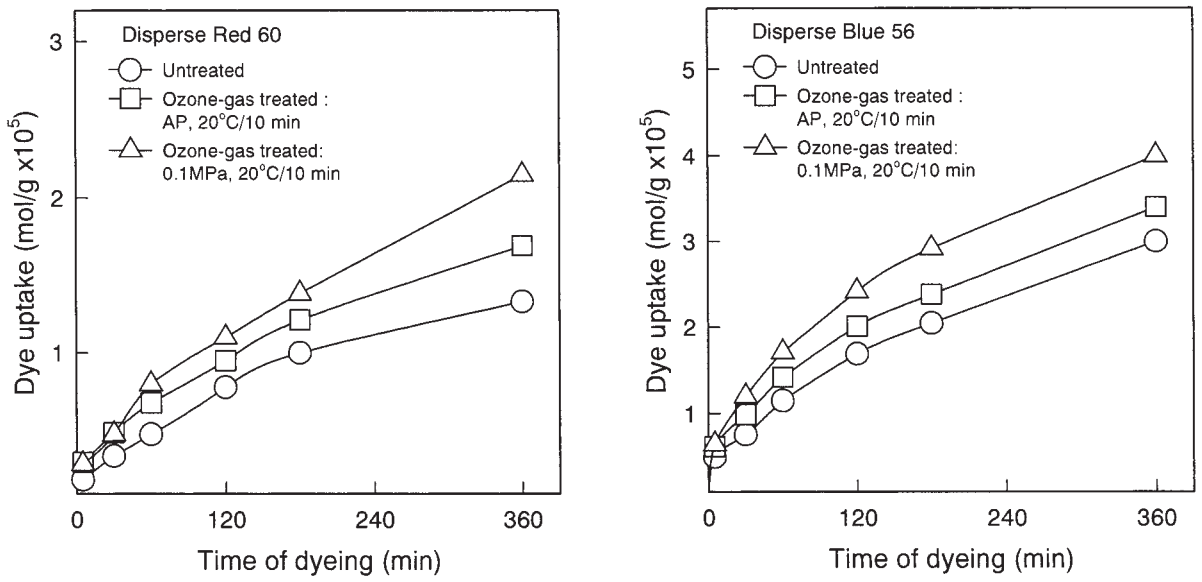



**Figure 3** Dyeing rates of disperse dyes on ozone-gas-treated polyester fabric.

ment in the surface tension of the fibers and naturally improve their wettability. Table III shows water penetration, moisture regain, and water absorption as a measure of the hydrophilicity and amorphous region of the fiber. Water penetration of the nylon 6 and polyester fabrics was accelerated considerably by the treatment, especially with increasing gas pressure. Both moisture regain and water absorption increased a little with treatment. We expected that an increase in the hydrophilic properties on the fiber surface would contribute to an improvement in the adhesion and vapor permeability of the fabric. Therefore, it was necessary to control the treatment conditions for each fiber to obtain a stable ozone-gas treatment.

Table IV shows the crystallinity of the nylon 6 and polyester fibers treated with ozone gas. The crystallinity of the polyester fiber increased a little with treatment. It seemed that the nylon 6 fiber also had an increase in crystallinity, as was evident from an increase in its density. Therefore, we expected that ozone-gas oxidization of the fabrics would cause a change not only in the fiber surface but also in the internal fine structure. An increase in the crystallinity might naturally influence the mechanical properties of the fabric.

## Dyeing properties

It is well known that the apparent dyeing rate and equilibrium dye uptake of nylon 6 and polyester fibers reflect the internal amorphous structure for dyeing with a disperse dye. The apparent dyeing rate of the ozone-gas-treated nylon 6 and polyester fabrics with Disperse Red 60 and Disperse Blue 56 are shown in Figures 2 and 3, respectively. The dyeing rates increased with treatment, especially for the polyester fabric. The equilibrium dye uptakes of the treated fabrics are shown in Table V. The equilibrium dye

**TABLE V**
**Equilibrium Dye Uptake of Disperse Dyes on Nylon 6 and Polyester Fabrics Treated with Ozone Gas**

| Treatment | Equilibrium dye uptake (mol/g × $10^5$) | |
|---|---|---|
| | Red 60 | Blue 56 |
| Nylon 6 fabric | | |
| Untreated | 1.09 | 5.01 |
| Ozone-gas treated | | |
| AP, 20°C/10 min | 1.13 | 5.28 |
| Polyester fabric | | |
| Untreated | 4.37 | 6.80 |
| Ozone-gas treated | | |
| AP, 20°C/10 min | 4.87 | 7.10 |
| 0.1 MPa, 20°C/10 min | 5.05 | 7.15 |

**TABLE VI**
**Time of Half-Dyeing of Disperse Dyes on Nylon 6 and Polyester Fabrics Treated with Ozone Gas**

| Treatment | Time of half-dyeing (min) | |
|---|---|---|
| | Red 60 | Blue 56 |
| Nylon 6 fabric | | |
| Untreated | 25 | 23 |
| Ozone-gas treated | | |
| AP, 20°C/10 min | 12 | 10 |
| Polyester fabric | | |
| Untreated | 863 | 538 |
| Ozone-gas treated | | |
| AP, 20°C/10 min | 826 | 431 |
| 0.1 MPa, 20°C/10 min | 660 | 282 |

**TABLE VII**
**KES Shearing Parameters of Ozone-Gas Treated Nylon 6 and Polyester Fabrics**

| Treatment | *G* (gf/cm °) | *2HG* (gf/cm) | *2HG5* (gf/cm) |
|---|---|---|---|
| Nylon 6 fabric | | | |
| Untreated | 0.38 | 0.68 | 1.54 |
| Ozone-gas treated | | | |
| AP, 20°C/10 min | 0.51 | 0.83 | 2.29 |
| 0.1 MPa, 20°C/10 min | 0.53 | 0.72 | 2.28 |
| Polyester fabric | | | |
| Untreated | 1.00 | 0.42 | 4.47 |
| Ozone-gas treated | | | |
| AP, 20°C/10 min | 1.77 | 0.68 | 6.14 |
| 0.1 MPa, 20°C/10 min | 1.22 | 0.77 | 6.17 |

uptake also improved, which was the same as that of the dyeing rate. As a result, time of the half-dyeing, as a matter of course, decreased clearly, as shown in Table VI. The dyeing properties of the nylon 6 and polyester fabrics were improved, despite an increase in crystallinity by the ozone-gas treatment. In previous articles, we reported on the solvent-assisted dyeing of polyester and nylon 6 fibers.[10,11] Polyester and nylon 6 fibers were pretreated with a benzyl alcohol/water solution, and then, the fibers were dyed with disperse dyes. The rate and equilibrium dye uptake increased despite an increase in the crystallinity; this result was the same as that of the ozone-gas treatment. Therefore, it is clear that ozone-gas treatment brought about an increase not only in the crystallinity but also in the amorphous region and contributed to the improvement of the dyeing properties.

From the results, it is obvious that the ozone-gas treatment of the nylon 6 and polyester fabrics caused a modification not only on the fiber surface but also in the internal fine structures, such as the crystallinity and the amorphous region; this was related to the dyeing behaviors, especially for the polyester fiber.

### Shearing properties

Table VII shows the shearing properties for the nylon 6 and polyester fabrics treated with ozone gas with various treatment conditions. *G*, 2*HG*, and 2*HG*5 of the polyester increased a little with ozone-gas treatment, regardless of the treatment conditions. Also, the *G*, 2*HG*, and 2*HG*5 parameters of the nylon 6 fabric increased just like those of the polyester fabric. Therefore, it was clear that the treatment of the nylon 6 and polyester fabrics caused the fabric hand to be much more crisp. However, the effect was much greater for the polyester fabric. In addition to the change in the internal structure by treatment, the —COH and —COOH hydrophilic groups taken up on the fiber surface, as a matter of course, contributed to an increases in the cohesion force between fibers, or yarns, because of an increase in the surface tension and frictional properties. As the results, the *G*, 2*HG*, and 2*HG*5 shearing parameters of the fabric increased a little with treatment, and the shearing deformation between yarns was controlled.

## CONCLUSIONS

Nylon 6 and polyester fabrics were treated with ozone gas, with conditions such as the gas pressure and the time varied. The $O_{1s}$ relative intensity, as measured by ESCA, increased apparently for nylon 6 and polyester fabrics. Oxygen was incorporated in the form of —COH and —COOH. As the results, water penetration into the fabric was accelerated just as in wool and silk fabrics.

Ozone-gas treatment of the nylon 6 and polyester fabrics brought about not only changes in the surface wettability but also changes in the internal fine structure, that is, in the crystalline and amorphous regions, especially for polyester fiber. As a result, the moisture regain, water absorption, and dyeing properties increased despite an increase in the crystallinity. The KES shearing parameters, *G*, 2*HG*, and 2*HG*5, of the fabrics treated with ozone gas increased compared with the untreated fabric. Therefore, it seemed that the ozone-gas treatment of the nylon 6 and polyester fabrics caused a change not only in their hydrophilic properties but also in their internal fine structure (the crystallinity and dyeing properties). Furthermore, ozone-gas treatment of the nylon 6 and polyester fabrics brought about little change in the mechanical properties and affected the crisp hand of the fabric.

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