

Ozone-Gas Treatment of Cationic Dyeable Polyester and Poly(butylene terephthalate) Fibers

Myung Sun Lee,¹ Muncheul Lee,¹ Tomiji Wakida,² Masumi Saito,² Takumi Yamashiro,³ Kenji Nishi,⁴ Goichi Inoue,⁵ Shinzo Ishida⁵

¹Department of Textile Engineering, Pusan National University, Pusan 609-735, South Korea

²Department of Home Economics, Gifu Women's University, Taromaru, Gifu 501-2592, Japan

³Kyoto Municipal Industrial Research Institute, Kamikyo-ku, Kyoto 602-0898, Japan

⁴Meisei Chemical Works, Sakyo-ku, Kyoto 615-8666, Japan

⁵Iwatani International Corporation, Ltd., Moriyama, Shiga 524-0041, Japan

Received 9 August 2006; accepted 29 November 2006

DOI 10.1002/app.25978

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Cationic dyeable polyester and poly(butylene terephthalate) fabrics were treated with ozone gas under atmospheric pressure and at a pressure of 0.1 MPa. The effect of the ozone-gas treatment was investigated on the basis of electron spectroscopy for chemical analysis, Fourier transform infrared spectrum, X-ray diffraction, moisture regain, water absorption, and dyeing properties. The ozone-gas treatment caused an increase in the oxygen content of each fiber. From the wave separation of C_{1s}, the oxygen was incorporated in the form of —CO— and —COO— on the fiber surface, and also, despite an increase in the water absorption, the fiber density as an index of crystallinity increased a little with the treatment. As the result, we concluded that the treatment caused a change

not only on the fiber surface but also in the internal structure of both fibers. Then, it seemed that the treatment brought about an effect on the dyeing properties. The apparent dyeing rate with the cationic dye increased remarkably with the ozone-gas treatment, whereas that with the disperse dye increased slightly. Therefore, it was clear that the ozone-gas treatment caused a change not only in the fine structure but also in the dyeing behavior. These phenomena were the same as those of poly(ethylene terephthalate) fibers. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 2423–2429, 2007

Key words: dyes/pigments; ESCA/XPS; FTIR; modification; polyesters

INTRODUCTION

Polyester fiber has been used widely in the textile industry, but it is not always possible to obtain bright and vivid shades because of its high refractive index. It is difficult to dye deeply due to its high crystallinity and high hydrophobicity. It is well known that cationic dyeable polyester (CDP) fibers have overcome the problem of dull color compared to regular polyester fibers. Furthermore, these fibers can be dyed under atmospheric pressure (AP). They are also available for energy conservation.^{1,2} On the other hand, poly(butylene terephthalate) (PBT) has wide engineering applications because of the higher crystallization rate than that of poly(ethylene terephthalate) (PET), and also, PBT is more suitable for injection molding.³ PBT has a relatively lower glass-transition temperature, lower melting point, higher crystallization rate, and lower maximum attainable crystallinity than PET fibers.^{4,5} Ozone-gas treatment has had interest in gas-phase textile finishing.^{6–8} Recently, we have studied ammonia-gas and ozone-gas treatments of textile fabrics. In pre-

vious articles, we reported the ammonia-gas treatment of silk fiber⁹ and ozone gas treatments of wool,¹⁰ nylon 6, and polyester fabrics.¹¹ The treatment took in oxygen in the form of —CO— and —COO— on the fiber surface. As the result, the wettability, apparent dyeing rate, and equilibrium dye uptake increased apparently. Therefore, it seems that ozone-gas treatment causes a change not only on the surface but also in the internal structure, such as in the crystallite and amorphous regions of the fiber.

Furthermore, in this study, CDP and PBT fabrics were treated with ozone gas under various conditions. The results were evaluated on the basis of the X-ray diffraction, electron spectroscopy for chemical analysis (ESCA), and dyeing properties.

EXPERIMENTAL

Materials

CDP (182 g/m²), which contained 5-sulfoisophthalic acid as a cationic dyeing site, and PBT (218 g/m²) knitted fabrics were used as materials. Ozone-gas treatment was carried out with the same equipment that was used in a previous study¹² for 10 min at AP and at 0.1 MPa.

Correspondence to: M. Lee (leemc@pusan.ac.kr).

Physical properties

ESCA of the treated CDP and PBT fabrics was carried out with a VG Scientific ESCALAB 250 spectrometer (West Sussex, England). From the wide-scanning ESCA spectra, the relative intensities of the C_{1s} and O_{1s} were determined. Furthermore, to elucidate the details of the chemical composition, curve fitting of the C_{1s} spectra was performed, and relative components of $-CH$, $-CO-$, and $-COO-$ were determined. Fourier transform infrared (FTIR) spectroscopic measurement was performed with a Nicolet Impact 400D FTIR spectrometer (Madison, WI) by the KBr pellet method. The X-ray refraction curve was obtained with a Rigaku Denki III D-Max (Tokyo, Japan). Also, as a measure of the internal compactness in relation to crystallinity, density was measured by means of the density gradient column method. Moisture regain and water absorption were measured according to the following procedure: the fabric was immersed in water for 24 h

and then centrifuged for 20 min at 3000 rpm (W_1). Subsequently, the fabric was kept for 48 h at 65% RH (W_2) and then dried for 3 h at 105°C (W_0). Moisture regain and water absorption were calculated with the following equations:¹²

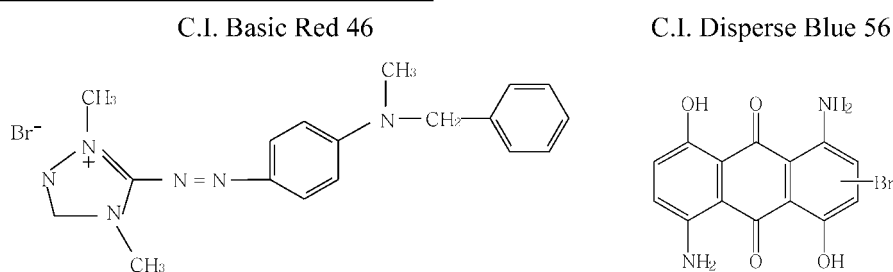
$$\text{Moisture regain (\%)} = ((W_2 - W_0)/W_0) \times 100$$

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

where W_1 is the weight of the centrifuged sample, W_2 is the weight of the water absorbed sample, and W_0 is the absolute dry weight of the sample.

Dyeing and color measurement

The treated CDP knitted fabrics were dyed with a cationic dye, C. I. Basic Red 46, and a disperse dye, C. I. Disperse Blue 56:



The dyebath was adjusted to pH 4.0 for the cationic dye and pH 5.0 for the disperse dye with acetic acid and sodium acetate buffers (1 : 1). The initial dye concentration in dyeing rate and equilibrium dye uptake was prepared to 4×10^{-4} mol/L for the two dyes. Dyeing was carried out at 100°C at a liquor ratio of 500 : 1, and the equilibrium dye uptake was obtained with dyeing for 24 h. The fabrics were extracted with 100% dimethylformamide, and the dye uptake was determined photometrically.

Color measurement of the dyed fabric was done with a MacBeth Color Eye 3100, and K/S value in Kubelka-Munk equation (K: absorption coefficient; S: scattering coefficient) and lightness (L^*) were obtained.

Lightfastness test

The lightfastness test was carried out in accordance with ISO 105-B02. The samples dyed with cationic and disperse dyes for 60 min at 100°C were exposed to a xenon arc lamp for 120 h.

RESULTS AND DISCUSSION

ESCA

Ozone gas is effective method for oxidizing organic materials. As reported in a previous article,¹¹ PET

fiber increases O_{1s} intensity by the ozone-gas treatment. Treatment is expected to cause oxidation of the fiber surface and lead to the chemical modification of the fiber, especially the hydrophobic fiber. Table I shows the ESCA wide-scan relative intensity of C_{1s} and O_{1s} of ozone-gas-treated CDP and PBT fabrics, respectively. The O_{1s} intensity corresponds to the relative functional oxygen component on the fiber surface. To elucidate the details of oxygen on

TABLE I
Relative Intensities of C_{1s} and O_{1s} in the Wide-Scanning ESCA Analysis of CDP and PBT Fabrics Treated with Ozone Gas

Treatment	Surface chemical composition (%)	
	C_{1s}	O_{1s}
CDP		
Untreated	74.1	25.9
Ozone-gas-treated		
AP, 20°C/10 min	73.4	26.6
0.1 MPa, 20°C/10 min	71.4	28.6
PBT		
Untreated	78.3	21.7
Ozone-gas-treated		
AP, 20°C/10 min	74.8	25.2
0.1 MPa, 20°C/10 min	74.9	25.1

TABLE II
Wave Separation of the C_{1s} Spectra of CDP and PBT Fabrics Treated with Ozone Gas

Treatment	Relative peak area (%)		
	-CH (285.0 eV)	-CO- (286.5 eV)	-COO- (289.0 eV)
CDP			
Untreated	67.4	22.9	9.7
Ozone-gas-treated			
AP, 20°C/10 min	55.9	31.4	12.7
0.1 MPa, 20°C/10 min	47.2	40.2	12.6
PBT			
Untreated	72.9	15.2	11.9
Ozone-gas-treated			
AP, 20°C/10 min	66.4	20.3	13.3
0.1 MPa, 20°C/10 min	62.3	25.6	12.1

the fiber surface, curve fitting of the C_{1s} spectra for the fabrics was done, and -CH, -CO- and -COO- peaks corresponding to 285.0, 286.5, and 289.0 eV are summarized in Table II. The -CO- and -COO- contents were increased by the treatment. From the results, it is clear that polymer surface of the CDP and PBT fibers were oxidized by the ozone-gas treatment. So, from the C_{1s} wave separation, it was obvious that an increase in the O_{1s} intensity contributed to an increase in the -CO- and -COO- functional groups. As a result, it seems that a change in the fine structure influenced the dyeing, adhesion, and mechanical properties.

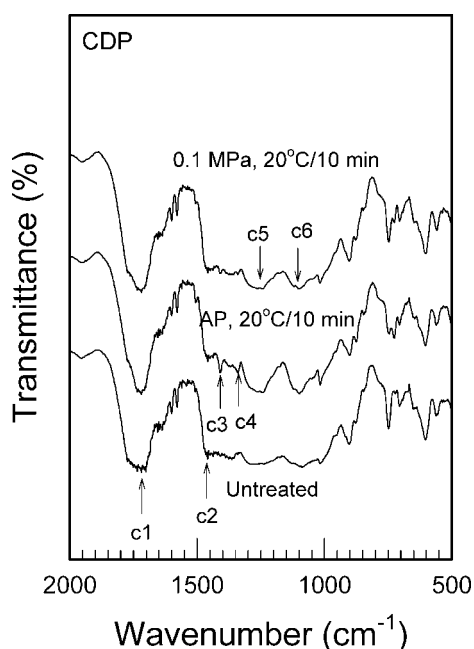


Figure 1 FTIR spectra of untreated and ozone-gas-treated CDP fiber.

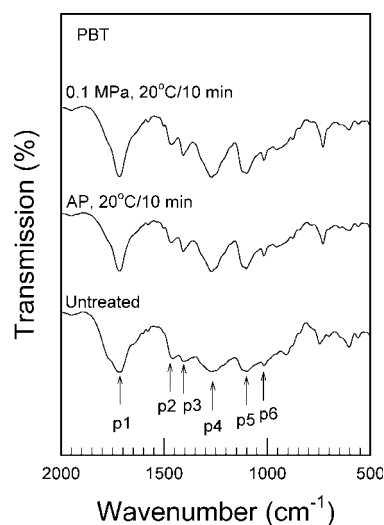


Figure 2 FTIR spectra of untreated and ozone-gas-treated PBT fiber.

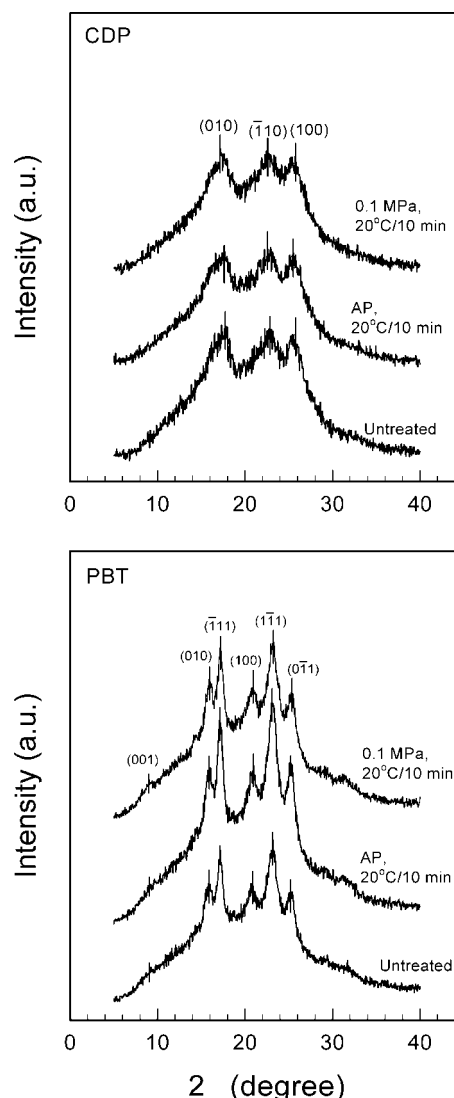


Figure 3 X-ray diffraction profiles of ozone-gas-treated CDP and PBT fibers.

FTIR spectra

Figure 1 shows the FTIR spectra of CDP fabrics treated with ozone gas. Generally, carboxylic acid salts have a band in the region $1440\text{--}1335\text{ cm}^{-1}$ due to symmetric stretching vibration of --COO^- , which is of medium intensity and broad, and generally has two or three peaks;¹³ the c3 and c4 peaks correspond to these peaks. So, it seems that ozone-gas treatment introduced oxygen in the form of --COO^- onto the CDP fiber surface.

As shown in Figure 2, for PBT fiber, p1 included the C=O stretching vibrations in carboxylic acid at 1720 cm^{-1} and became sharp with the ozone-gas treatment. p2 and p3 were assigned to a C--H bending vibration and wagging at 1465 and 1403 cm^{-1} , respectively. Two peaks, p4 and p5, appeared due to symmetric stretching vibrations of ester --COO-- .

These peaks turned sharply with ozone-gas treatment. The C--C stretching in the benzene ring appeared at 1025 cm^{-1} (p6). Particularly, p2 and p6 denoted α -form crystals,^{14,15} and the increase in the intensity of these peaks meant that the α -form rate was increased by the ozone-gas treatment.

X-ray diffraction and density

Figures 3 and 4 show wide-angle X-ray diffraction equatorial scans for ozone-gas-treated CDP and PBT fibers, respectively. CDP fiber had crystalline reflections at $2\theta = 17.8, 23.1,$ and 26.4° , which were equivalent to (010), (1 $\bar{1}$ 0), and (100), respectively. The crystallite form was not changed by the ozone-gas treatment. On the other hand, PBT fiber had crystalline reflections at $2\theta = 9.2, 15.8, 17.2, 20.5,$ and 23.5° ,

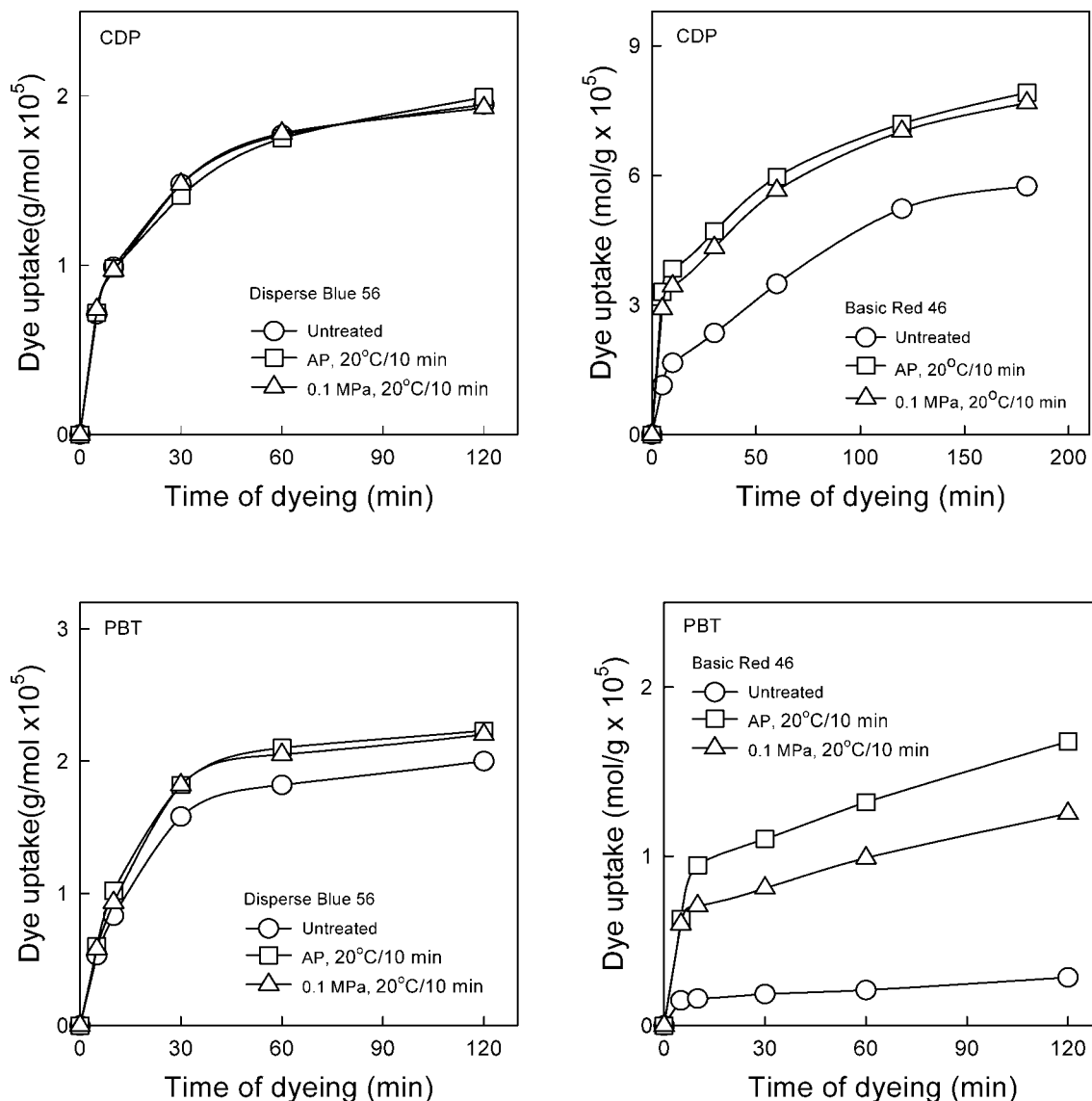


Figure 4 Dyeing rates of disperse and cationic dyes for ozone-gas-treated CDP and PBT fabrics.

TABLE III
Density of CDP and PBT Fibers Treated with Ozone Gas

Treatment	Density (g/cm ³)	
	CDP	PBT
Untreated	1.319	1.322
Ozone-gas-treated		
AP, 20°C/10 min	1.320	1.325
0.1 MPa, 20°C/10 min	1.323	1.325

which were equivalent to (001), (010), ($\bar{1}\bar{1}\bar{1}$), (100), and ($\bar{1}\bar{1}\bar{1}$) of the α -form crystallite. It is well known that there are α - and β -form crystallites in PBT fibers.¹⁶ However, it is difficult to calculate the crystallinity by means of the density method because the crystallite densities of the α and β types are not known. Table III shows the densities of the CDP and PBT fibers treated with ozone gas. As a measure of the compactness of the fiber, density increased with ozone-gas treatment. These results correspond well to the intensity increases of p2 and p6 in the FTIR spectra with ozone-gas treatment.

Moisture regain and water absorption

Table IV shows the moisture regain and water absorption of the CDP and PBT fabrics treated with the ozone gas. The moisture regain of CDP increased only a little with the treatment. The water absorption of CDP fabric showed almost no change with the treatment, whereas for PBT, moisture regain and water absorption clearly increased with the treatment. This result corresponded well to oxygen quantities measured by ESCA. Therefore, it seemed that changes in the amorphous structure caused by the treatment played a great role not only in the water absorption but also in the dyeing properties.

Dyeing properties

The apparent dyeing rates of the cationic and disperse dyes in the ozone-gas-treated CDP and fabrics

TABLE IV
Effect of Ozone-Gas Treatment on the Moisture Regain and Water Absorption of CDP and PBT Fabrics

Treatment	Moisture regain (%)	Water absorption (%)
CDP		
Untreated	0.89	1.65
Ozone-gas-treated		
AP, 20°C/10 min	0.94	1.64
0.1 MPa, 20°C/10 min	0.90	1.65
PBT		
Untreated	0.20	0.63
Ozone-gas-treated		
AP, 20°C/10 min	0.42	2.62
0.1 MPa, 20°C/10 min	0.38	2.47

TABLE V
Effect of Ozone-Gas Pretreatment on the Color Depth of CDP and PBT Fabrics Dyed with Basic Blue 3

Treatment	L*	K/S
CDP		
Untreated	75.61	1.13
Ozone-gas-treated	65.20	3.91
PBT		
Untreated	82.79	0.12
Ozone-gas-treated	69.54	2.23

Dyeing was carried out at 50°C for 5 min at a liquid ratio of 100 : 1. After dyeing, the fabric was soaped with anionic detergent.

are shown in Figure 4. The apparent dyeing rate of the fabric with cationic dye was accelerated considerably by the ozone-gas treatment, despite an increase in the fiber density.¹¹ On the other hand, the dyeing rate with disperse dye was only slightly changed. In PBT fabric, the apparent dyeing rates of both the cationic and disperse dyes increased considerably with the treatment. From these results, it is clear that oxygen was taken as a result of the treatment and was in the form of $-\text{COO}-$ in the fiber, and the group changed to $-\text{COO}^-$ in the dye-bath, which could be bound with the cationic ion of the cationic dye.

The apparent dyeing rate of CDP and PBT increased apparently with the ozone-gas treatment independently in the cationic and disperse dyes. CDP fiber has a sulfonic acid group itself as a dyeing site for cationic dye. The ozone-gas treatment of PBT fiber increased the dye uptake; nevertheless, PBT fiber has no cationic dyeing site itself. Therefore, it was clear that carboxylate group ($-\text{COO}^-$) contributed to the dye uptake of PBT. Table V shows the color measurement L^* and K/S of CDP and PBT dyed with Basic Blue 3 at 50°C for 5 min. The untreated CDP fabric was dyed a little, whereas

TABLE VI
Equilibrium Dye Uptake of Cationic and Disperse Dyes for Ozone-Gas-Treated CDP and PBT Fabrics

Treatment	Equilibrium dye uptake (mol/g $\times 10^3$)	
	Basic Red 46	Disperse Blue 56
CDP		
Untreated	16.91	2.95
Ozone-gas-treated		
AP, 20°C/10 min	16.85	2.97
0.1 MPa, 20°C/10 min	16.76	2.95
PBT		
Untreated	0.89	2.27
Ozone-gas-treated		
AP, 20°C/10 min	1.97	3.21
0.1 MPa, 20°C/10 min	1.80	3.16

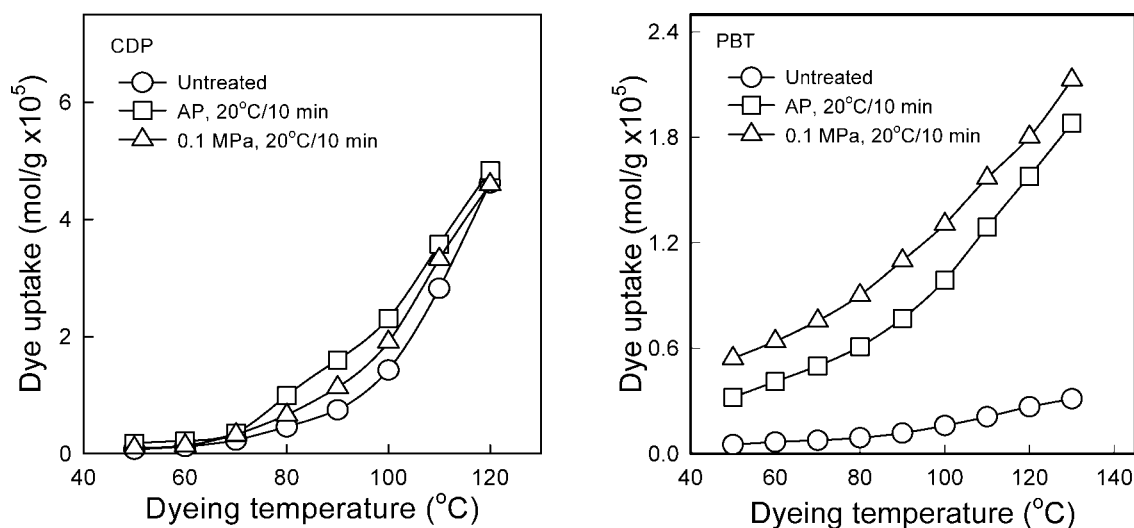


Figure 5 Relationship between dye uptake and dyeing temperature of Basic Red 46 for ozone-gas-treated CDP and PBT fabrics.

untreated PBT was dyed almost negligibly. Nevertheless, the color depth of the ozone-gas-treated CDP and PBT fabrics increased not only for cationic but also for disperse dyeings. Therefore, it was clear that the dyeing acceleration of CDP and PBT by the ozone-gas treatment was caused by the incorporation of the $-\text{COO}-$ group.

The equilibrium dye uptake of the treated fabrics is shown in Table VI. It is well known that equilibrium dye uptake reflects the amorphous internal volume in relation to dyeing with cationic and disperse dyes. Although the ozone-gas treatment did not change the equilibrium dye uptake for both dyes in the CDP fabric, in the PBT fabric, it increased apparently for cationic and disperse dyes.

As an illustration of the dyeing transition behaviors of the CDP and PBT fabrics, the relationship between the dye uptake of Basic Red 46 and dyeing

temperature is shown in Figure 5. Dyeing was done for 10 min at each temperature. The dyeing transition temperature decreased with the ozone-gas treatment. Therefore, it was clear that ozone-gas treatment of the CDP and PBT fabrics induced the relaxation of the fiber structure, and the effect contributed to an increase in the dyeing rate.

The effect of ozone-gas treatment on the lightfastness of the samples dyed with Basic Red 46 and Disperse Blue 56 is shown in Table VII. It is well known that lightfastness of cationic dye is inferior to that of disperse dye. It seemed that the lightfastness was not influenced by the ozone-gas treatment.

CONCLUSIONS

CDP and PBT knitted fabric were treated with ozone gas under AP and 0.1 MPa, and the effect was investigated by ESCA analysis, X-ray refraction, FTIR measurement, and dyeing properties with ozone-gas treatment. The ozone-gas treatment induced an increase in O_{1s} intensity. Oxygen was incorporated in the form of $-\text{OH}$, $-\text{COOH}$, which led to an increase in moisture regain and water absorption. The treatment caused an acceleration in the dyeing rate for the cationic and disperse dyes, especially for the cationic dye. Despite an increase in the fiber density with the treatment, the equilibrium dye uptake with cationic and disperse dyes increased for PBT, but it did not increase for CDP fibers.

References

1. Pal, S. K.; Gandhi, R. S.; Kothari, V. K. *J Appl Polym Sci* 1996, 61, 401.
2. Teli, M. D.; Rao, B. R. *J. Soc Dyers Colour* 1996, 112, 239.

TABLE VII
Lightfastness of Cationic and Disperse Dyes for Ozone-Gas-Treated CDP and PBT Fabrics

Treatment	Change of shade (gray scale)	
	Basic Red 46	Disperse Blue 56
CDP		
Untreated	2	4
Ozone-gas-treated		
AP, 20°C/10 min	4	4
0.1 MPa, 20°C/10 min	3	4
PBT		
Untreated	—	4
Ozone-gas-treated		
AP, 20°C/10 min	2	4
0.1 MPa, 20°C/10 min	2	4

Dyeing was carried out with 3% owf for both dyes.

3. Yasuniwa, M.; Tsubakihara, S.; Ohoshita, K.; Tokudome, S. *J Polym Sci Part B: Polym Phys* 2001, 39, 2005.
4. Gilbert, M.; Hybart, F. J. *Polymer* 1972, 13, 327.
5. Gilbert, M.; Hybart, F. J. *Polymer* 1974, 15, 408.
6. Karakawa, T.; Umehara, R.; Ichimura, H.; Nakase, K.; Ohshima, K. *Sen'I Gakkaishi* 2002, 58, 135.
7. Kashihara, T. Preprint of Lecture at 120 Committee of Fiber and Polymer Functional Finishing of Japan Science Promotion; Tokyo, Japan, June 2003; p 28.
8. Yamashiro, T.; Tani, T. Technical Report of Dyeing Institute of Kyoto City; Dyeing Institute of Kyoto City: Kyoto, Japan, 1998; p 89.
9. Lee, M. S.; Lee, M.; Tokuyama, T.; Wakida, T.; Inoue, G. *J Appl Polym Sci* 2006, 101, 3487.
10. Wakida, T.; Lee, M.; Jeon, J. H.; Tokuyama, T.; Kuriyama, H.; Ishida, S. *Sen'I Gakkaishi* 2004, 60, 213.
11. Lee, M.; Lee, M. S.; Wakida, T.; Tokuyama, T.; Inoue, G.; Ishida, S.; Itazu, T.; Miyaji, Y. *J Appl Polym Sci* 2006, 100, 1344.
12. Wakida, T.; Lee, M.; Niu, S.; Yanai, Y.; Yoshioka, H.; Kobayashi, S.; Bae, S.; Kim, K. J. *Soc Dyers Colour.*, 1995, 111, 154.
13. Socrates, G. *Infrared Characteristic Group Frequencies Table and Chart*, 2nd ed.; Wiley: New York, p 91.
14. Ward, I. M.; Wilding, M. A. *Polymer* 1977, 18, 327.
15. Stambaugh, B.; Lando, J. B.; Koenig, J. L. *J Polym Sci Polym Phys Ed* 1979, 17, 1063.
16. Roebuck, J.; Jakeways, R.; Ward, M. *Polymer* 1992, 33, 227.