Chemical Structure Change of a KrF-Laser Irradiated PET **Fiber Surface**

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ABSTRACT: Laser ablation of a poly(ethylene terephthalate) fabric with an excimer laser beam (248 nm) was analyzed by color tests, and the chemical structure change of the surface was studied. This analysis suggests the possibility of the formation of both OH and CHO groups on the poly(ethylene terephthalate) surface. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 2027-2031, 1999

Key words: laser ablation; PET

INTRODUCTION

Variou studies of changes on the surfaces of high polymers due to excimer laser irradiation have been conducted since laser ablation was report ed^{1-3} for the first time in 1982.

Subsequently, there have been many reports of surface modification⁴⁻⁹ when excimer lasers irradiate polymer fibers and films. The special feature of our research is that we have also made use of a photochemical process that is specific to the excimer laser, an ultraviolet light with sharp monochromatism and high intensity, and have investigated the processing and modification of the surface of poly(ethylene terephthalate) (PET) films and fibers.^{10–13} In a previous article, fragmentation of PET by laser ablation was studied to clarify the mechanism.¹⁴

Important quantities for textile processing, which may be affected by the ultraviolet laserinduced surface modification, are the wetting behavior and adhesion properties of a fiber or a fabric, which not only affect processing, but also

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define a textile's properties in certain applications. A very favorable coloration process is dyeing using dyestuffs. This technique has a great impact in the dyeing technology of fabrics.

In this article, we try to clarify visually the chemical structure change of the PET fiber surface after/during laser ablation, applied with the dyeing method.

EXPERIMENTAL

Materials

The PET fiber used in this experiment was a 50 denier and 75 denier drawn yarn with a normal degree of polymerization ($M_n = 14,900$, carboxyl end-groups [—COOH] value of 46×10^{-6} eq g^{-1}) made by Teijin Ltd. and a plain weave fabric woven by selecting a 50 denier yarn at 105 threads/inch for warp. For the weft, a 75 denier yarn at 83 threads/inch was used.

The surface of sample fabrics was cleaned in ethyl alcohol and distilled water for 10 min each and dried for 24 h in a 30°C vacuum dryer before the experiment.

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C.I. Disperse Blue 79



C.I. Direct Black 19

Figure 1 Chemical structure of dyestuff, applied in this experiment.

Irradiation with Excimer Laser

Irradiation was conducted with a KrF excimer laser (248 nm) (Lambda-Physik Model LPX120icc) filled with a mixture of Kr, Ne, and F_2 gases.

Dyeing After Ablation

By the Conventional Method

The sample fabric was irradiated at a specified irradiation energy (fluence: 30, 50, 100, 150, 200, and 340 mJ cm⁻²). The number of irradiated pulses was 10 shots. These fabrics were put into the disperse dyestuff (C. I. Disperse Blue 79) resolved solution at 130°C for 60 min and were dyed. They were then washed with hot water (at 80°C) for 10 min.

With Direct Dyestuff

The sample fabric was irradiated at a specified irradiation energy (fluence: 10, 30, 50, and 100 mJ cm⁻²). The number of irradiated pulses was 10 shots. Half of these fabrics were put into the direct dyestuff (C. I. Direct Black 19) resolved solution at 90°C for 60 min and were dyed. The other half were at first dipped in a glycidyl-ether containing water solution, squeezed, and then cured in an oven at 180°C for 3 min. They were then put into the same dyestuff solution and dyed under the same conditions. Both of the samples dyed from the same fabric were washed with hot water (at 80°C) for 10 min.

Chemical structure of dyestuffs, applied in this experiment, are shown in Figure 1.

Dyeing During Ablation

The sample fabric was put into Schiff's solution and was irradiated at a specified irradiation energy (fluence: 30 mJ cm^{-2}). The number of irradiated pulses was 30 shots.

After irradiation, the fabric was washed with hot water (at 80°C) for 10 min.

Estimation of Dyeing Properties

The deepness of dyed color was estimated using the K/S factor, according to the Kubelka–Munk equation¹⁵:

$$K/S = (1 - R_{\infty})^2/(2R_{\infty})$$

where K is absorption coefficient of light; S is scattering coefficient of light; and R_{∞} is reflectance at maximal absorption wavelength of visible light's reflection curve, measured by a spectrophotometer (Color-Eye 3100, Macbeth Co.). Note that the greater the estimation of the K/Sfactor, the more deeply dyed is the color of the PET fabric.

RESULTS AND DISCUSSION

Dyeing Behavior of the Ablated Fabric by a Disperse Dye

Using a conventional method of disperse dye (C. I. Disperse Blue 79) and after irradiation with KrF laser, Figure 2 shows the results of measuring the dyeing characteristic of PET fabric dyed in a blue. As the irradiation fluence increases, the dyed color tends to be darker (deeper). This is because tiny ripples are formed on the PET fiber surface by laser irradiation, and the color appears to be darker due to changes in the refractive index and reflectivity on the fiber surface as reported by Knittel and colleagues.¹⁶ Also, as reported previously,¹⁰ the amorphous ratio increases on the PET surface layer due to laser irradiation, and



Figure 2 Dyeing characteristic of PET fabric dyed in blue after KrF-laser irradiation.

 irradiation conditions
 none
 10mJ/cm²
 30mJ/cm²
 50mJ/cm²

 PET fabric
 10shots
 10shots
 10shots

 non treatment
 10shots
 10shots
 10shots

Dyed with C.I.Direct Black 19

Figure 3 Color tones of PET fabric dyed with black direct dye after KrF-laser irradiation.

the dye is more likely to diffuse, thereby, increasing the dye deposit. Although Knittel and colleagues¹⁶ reported that the dye deposit was not changed, the present result is contrary to their result. Moreover, because the dyeing performance is hardly changed if the dyed fabric is washed in hot water, it is supposed that the dye is firmly affixed in the structure of the PET. However, in a cotton fabric of the same structure and composition as the PET dyed fabric, by 100 times of friction by applying a load of 50 g cm^{-2} , the observed color tends to be pale as the energy increases when the laser irradiation energy exceeds a certain value. This is possibly because the ripples formed by irradiation are likely to deteriorate; and, as the energy increases, the surface is peeled off by friction.

Analysis of the Ablated Surface by Color Reaction

When dyeing PET fabrics, it is general to use a disperse dye and dye at a high temperature of $\sim 130^{\circ}$ C. However, if the PET surface is chemically changed by laser ablation and certain functional groups are formed, it should also be possible to dye by using alternatives to a disperse dye.

Accordingly, the presence or absence of the formation of an OH group was investigated by dyeing with a direct dye, and the presence or absence of a CHO group by dyeing with Schiff's base solution. Moreover, in the former case, to prove it possible to dye with a direct dye in the presence of an OH group, a comparative study of a PET fabric preliminarily treated with glycidyl ether (epoxy) was conducted.

Analysis of the Presence or Absence of the Formation of an OH Group—Dyeing with Direct Dye After Ablation

Figure 3 shows color tones of PET fabric dyed

Dyed with C.I.Direct Black 19



Figure 4 The *K*/*S* value obtained by measuring the fabric surface.

with black direct dye (C. I. Direct Black 19) after laser ablation in various conditions. It also shows the results of an epoxy-treated fabric. Figure 4 records the K/S value obtained by measuring these surfaces (this value expresses the degree of dyeing by reference to an undyed fabric; hence, the larger the figure, the deeper the color of the dyeing). As can readily be seen, the epoxy-treated fabric is dved relatively dark because of the OH group produced by opening the ring of the epoxy group; but, the untreated fabric does not develop a black color partly because the dyeing temperature is similar to that of ordinary cotton dyeing. However, as the ablation energy increases, it is observable that the colors are darkened in both fabrics. As a result of measurement, when the irradiation fluence is about to exceed the threshold ($\sim 30 \text{ mJ cm}^{-2}$ for PET), the K/S value begins to elevate. Figure 5 shows the results of measuring the absorption of dye using the colorimetric method of dissolv-



Figure 5 Absorption of dye using the colorimetric method.

	non treatment	Dyed after ablation	Dyed during ablation
non irradiated			
KrF irradiated		n an	

Dyed with Schiff's solution

KrF (248nm); 50mJ/cm², 10shots

Figure 6 Color tones of PET fabric dyed with Schiff's base solution.

ing the dyed fabrics in an *o*-chlorophenol solution. Along with the increase of ablation energy, it is observable that the absorption of the dye by the PET fabric is increased. In untreated PET, although the dye is not absorbed sufficiently to be dyed black, the amount of absorption tends to increase by laser irradiation, which suggests the possibility of the formation of an OH group, even if only slightly, on the PET surface.

Analysis of the Presence or Absence of the Formation of a CHO Group—Dyeing with Schiff's Base Solution in Ablation

In this case, color reaction was evaluated in Schiff's base solution which, of course, does not require heat for dyeing. Figure 6 shows color tones by immersing a PET fabric in Schiff's base solution after laser ablation, and by laser ablation of the PET fabric in a wet state by preliminary immersion in the solution. The colors are developed in both cases; but, when treated in a wet state, a deeper color is achieved. Quantifiable results are shown in Figure 7. It can be confirmed from the numerical values that the dyeing is deeper when treated in a wet state. It suggests



Dyed with Schiff's solution

Figure 7 *K/S* value obtained by measuring the fabric surface.



Figure 8 Reaction formula on the PET fiber surface by KrF-laser irradiation.

the possibility of the formation of a CHO group on the PET surface.

Changes in Chemical Structure on the PET Surface

Considering the results, changes on the PET surface by laser ablation were subsequently estimated.

As reported previously, on the PET surface, the amorphous rate is increased by laser ablation, the ratio of O atoms to C atoms in PET is lowered, a deoxidation-like reaction takes place; CO, CO₂, CH₂==CH₂ scatters from the surface layer; and a cyclic oligomer is formed. Moreover, as elucidated by the present experiment, it is estimated that OH and CHO groups are also formed. Formation of the CHO group seems to be caused by photoreaction, whereas formation of the OH group appears to be due to a decomposition reaction from momentary heat at the time of laser irradiation. Such a mode of reaction is shown in the reaction formula in Figure 8.

CONCLUSIONS

With respect to color reaction, and by means of KrF laser ablation, our research has attempted to analyze chemical changes of the surface of a PET fabric. After irradiation with energy above threshold levels, the possibility of the slight formation both OH and CHO groups on the PET surface have been recognized. By making the best use of this phenomenon, it is anticipated that it may be possible to expand the possibility of functional processing of fibers by postprocessing.

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