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Plasma Treatment of Silk Fabrics

for

Better Dyeability

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Silk fabrics were treated with 02, N2, and H. plasmas for deep dyeing and good color fastness to rubbing. C.I. (Color Index) Reactive Black 5 was used as a dye, and color deepness was evaluated by total K/S. All plasma-treated silk fabrics showed weight loss, especially by 02 plasma. Total K/S of dyed silk fabrics treated at 60 Pa of all plasmas was improved greatly. Total K/S increased with increasing plasma treatment time, weight loss of the fabrics in the treatment, and dye concentration in dyeing. They gained greater total K/S even dyed in 6% of dye concentration compared with untreated one dyed in 10%. Color fastness to wetrubbing of silk fabrics was not improved by plasma treatment. However, most of them were still within the level for commercial use.

Keywords: plasma treatment, silk fabrics, dyeing, K/5, color fastness to wet rubbing

1. Introduction
Plasma surface treatment of fiber or fabrics has

been applied in many fields for a long time [1-5]. One of the main purposes of the treatment is, in analogy with most of the other materials, the improvement of the surface energy by using hydrophilic-natured plasma. Higher surface energy makes adhesivity or printability better for plastics or any solid materials.
As an application for fabrics (fiber), for example, both organic and inorganic fabrics (fiber) with improved adhesivity or compatibility against plastics by plasma treatment are used for fiber-reinforced plastics (FRP), which could raise their performance [6-14].
Another and more important application in plasma treatment of fabrics utilizing higher surface energy is the improvement of dyeability for clothing use. For the purpose of dyeability or color deepening, plasma treatments for many kinds of fabrics, such as poly(ethylene terephthalate), nylon-6, nylon-66, aramid, and wool, have been reported [15-17]. In

these researches, chemical interaction between fiber and dye seems to be rather important than just surface energy. In addition, as far as color deepening is concerned, surface morphology of fiber caused by plasma etching is also crucial.
Until recently, reports on plasma treatment of silk were not too many. With increasing popularity of natural products, demands of silk for not only clothing use but also personal-care products and foods have been increasing lately.
Zhang graft polymerized acrylamide on silk fabrics surface by plasma-induced method, and analyzed the surface [18].
Nishikawa et al. prepared fibroin film and treated with CF4 plasma [19]. They intended fluorination of the film, but they could not obtain very hydrophobic surface as they expected. After the immersion of the plasma-treated films in water, they found hydrolysis of peptide bonds mainly caused by F in the plasma.
Selli et al. treated silk fabrics with SF6 plasma,
and they claim that F replaced H easily and the

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fluorination was effective [20].
Nakano et al, measured surface area of 02-

plasma-treated silk fabrics with a modified-BET apparatus that they have developed [21]. It will be very interesting if a relationship between the surface area and color deepness is revealed.
As the use of silk fabrics increases, their defects have become clear. In addition to deeper dyeing, improvement of color fastness property is often required. In general, color fastness of silk is not satisfactory. When silk fabrics are rubbed with other clothing, dye on the silk transfers to the other cloths, which is called "color pollution".
In this study, we treated silk fabrics with 0, N2, and H2 plasmas in order to improve color deepness of dyed silk fabrics and improve color fastness to rubbing. The use of plasma technique, in which little waste is produced as a dry process, is also concerned with the "environment".

2. Experimental
2.1. Materials

Silk fabrics used in this study were provided by Chuo Sen-i Co. Silk threads with three 21-denier fibers each were woven into silk fabrics with the

densities of warp and woof 200 and 135 threads per 3.8 cm, respectively. After weaving, the silk fabrics were washed in a soap solution with Na2C03 for the removal of sericin. The fabrics were cut

into the size of 200 X 300 mm for plasma treatments. This length is required for the measurement of color fastness to wet rubbing although the area of the circle of about 200-mm diameter can be treated

uniformly.
Oy N~, and H2, obtained from Iwatani Sangyo, were used as plasma gases.
C.I . (Color Index) Reactive Black 5 (DyStar Inc., Remazol Black B) was used as a dye, of which structural formula is shown in Figure 1. Sodium sulfate, sodium carbonate (both from Wako Pure Chemical), and nonionic surfactant as a soaping agent (Heian Yushi Kagaku Industry, Soilless HC) were used in the dyeing and soaping processes. White cotton fabrics used for the test for color

fastness to wet rubbing was standard testing fabrics of Japanese Standards Association.

2.2. Plasma Treatment
Plasma treatment of silk fabrics was carried out

in a plasma treatment apparatus, manufactured by SST Inc., shown in Figure 2. Power electrode (aluminum, 150-mm d.), which is connected to an rf (13.56 MHz) generator via an automatic matching unit, is at the bottom of the reactor. Ground electrode is the whole plate of the top cover of the reactor. The gap between the electrodes was 50 mm.
A piece of silk fabrics was placed on the bottom electrode. The reactor was evacuated with a rotary vacuum pump for 10 min, then plasma gases were introduced into the reactor through a needle valve and the pressure was adjusted to predetermined values (60-400 Pa). The pressure of the system was monitored with a pirani gauge (Shinko Seiki, PG-MW2).
Plasma discharge power was fixed to 50 W. Plasma treatment time was varied up to 30 min. The bottom electrode was cooled with 25-°C circulating water during the treatment.
2.3. Measurement of Weight Loss
Weight of silk fabrics before and after plasma treatments was measured, and weight loss was calculated. All the fabrics samples were dried at 105 °C for 30 min prior to the measurement for the exclusion of the effect of absorbed water.

2.4. Surface Analysis
Chemical composition of plasma-treated silk fabrics surfaces was analyzed with X-ray photoelectron spectroscopy (XPS, Shimadzu,

Figure 2. Apparatus for the plasma surface treatment
of silk fabrics.

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ESCA-750). Surfaces of plasma-treated silk fabrics were observed with scanning electron microscope (SEM, Elionix, EXM-3500).
2.5. Dyeing
Plasma-treated silk fabrics were dyed in a 250-mL mixture solution of the dye, Na2SO4 (40 g/L), and Na2CO3 (4 g/L) at 50 °C for 90 min. Four sheets of plasma-treated fabrics were dyed at once. The amounts of the dye dissolved in the solution is normally 10% of the weight of fabrics to be dyed. In this study, we varied the amounts of the dye from 4% to 10%. Following the dyeing and rinsing with water, fabrics were cleaned with a 250-mL soap solution at 85 °C for 15 min that contains the soaping agent (2 g/L) and Na2CO3 (2 g/L). Finally, the fabrics were rinsed with large amounts of water and dried at room temperature.
2.6. Color Measurement

For the evaluation of color deepness of dyed silk fabrics, reflectance of visible light from 400 to 700 nm was measured at every 20 nm with a reflect meter (Kurabo, AUCOLOR-10a), and K/S value was obtained by Kubelka-Murk equation,
K/S= {(1 -R)2/2R}-{(1-R')2/2R'}
where R and R' are reflectance before and after

dyeing, respectively. K and S are absorption coefficient and reflection coefficient of fabrics, respectively. We take total K/S value, which is the summation of K/S at every 20 nm in the range between 400 and 700 nm, as an indication of color deepness.

2.7. Test for Color Fastness to Wet Rubbing
Test for color fastness to wet rubbing was performed witha friction tester (Daiei Kagaku Seiki) according to Japanese Industrial Standard (JIS) L0849II. As shown in Figure 3, a dyed test piece

of silk fabrics (30 X 300 mm) was placed on the bottom table, on which a rubbing piece of wet white cotton fabrics (50 X 50 mm) was pressed down with the load of 2 N. The table was moved back

and forth as the following conditions: one-way distance, 100 mm; speed, 100 mm/s; time, 200 s. After the test, dye on the dyed silk fabrics surface
was found to transfer to the white rubbing cotton

Figure 3. Friction tester for the test for color fastness to wet rubbing.

Figure 4. Weight loss of the silk fabrics after plasma treatment in various plasma conditions.

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fabrics slightly. Color fastness was evaluated by the color of the cotton fabrics and graded from Level 1 to Level 5 by human eye, according to JIS. Level 2-3, which indicates Level between 2 and 3, or greater is accepted for commercial use.
2.8. Friction Test

Friction coefficient of plasma-treated silk fabrics was measured with a surface tester (Kato Tech, KES-FB4). In this test, a piece of silk fabrics (200 X 200 mm) was set on a bottom table with a tension of 0.2 N/cm, on which ten pieces of piano wire fixed in parallel in the area of 5 X 5 mm were contacted with the load of 0.49 N. When the piano wire moved onthe fabrics, frictionforce was detected and friction coefficient was calculated.

3. Results and Discussion

3.1. Plasma Etching of Silk Fabrics
In plasma treatments with non-polymer-forming
gases, in general, etching of substrates is not negligible. In this study of plasma treatment of silk fabrics, also, etching was observed by weight loss of the fabrics and SEM observation.

Figure 4 shows weight loss of the silk fabrics after plasma treatment in various plasma conditions. In plasma treatments of those non-polymer-forming gases, weight loss of silk fabrics was observed in the most of plasma conditions. As a general trend,

in those figures, weight loss was greater at lower pressure (60 Pa), where etching takes place effectively because of the higher plasma energy density. Among those gases, naturally, the greatest weight loss was observed in 02 plasma.
SEM photographs of plasma-treated silk fabrics (60 Pa, 30 min) are shown in Figure 5. Photographs of those treated at 400 Pa were omitted because no

significant difference was observed compared with untreated one even by 02 plasma treatment.
The surface of untreated silk fabrics is very smooth, while those of plasma-treated ones are not. Obviously, that treated with 02 plasma at 60 Pa was etched the most and showing severe damage on the surface. The etching may not be limited to just surface, because the fibers became thinner. Those treated with N2 and H2 plasmas at 60 Pa also showed micropittings on the surface.
Although the surface roughness is not measured quantitatively, the roughness seems to have a correlation against the weight loss.
We also measured chemical composition and friction coefficient of the surface, but we will discuss
them in the following sections in connection with
dyeability and color fastness.
3.2. Dyeability of Plasma-Treated Silk Fabrics
3.2.1. Effect of Plasma Condition

Figure 6 shows total K/S of plasma-treated silk

Figu re 5. SEM photographs of plasma-treated silk fabrics at 60 Pa for 30 min. (a) Untreated, (b) 02, (c) N2, (d) H2 plasma.

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fabrics in various plasma conditions after dyed in 10% dye concentration. Only silk fabrics treated at 60 Pa showed improved total K/S, and a dependence of treatment time was found. Among three plasmas, 02 plasma showed the best total K/S: closed 400 by 30-min treatment, which is an outstanding value for silk fabrics.
Those treated at 200 and 400 Pa showed almost

no change of K/S from untreated one. This big

difference in K/S by pressure might havebeen caused by etching, as we indicated the previous section: lower pressure gains higher plasma energy density, which is preferable to etching.
3.2.2. Effect of Surface Chemical Composition After plasma treatment, chemical composition of silk fabrics surface was estimated from the results

of XPS measurement. After 02 plasma treatment, O/C increased greatly and N/C increased slightly. After N2 plasma treatment, both O/C and N/C increased slightly, while the both decreased slightly after H2 plasma. The dye used in this experiment (C.I. Reactive Black 5, shown in Fig.1) has many acidic and a basic functional groups. Therefore, more interaction between the dye and silk fabrics is expected if there are more functional groups on the silk surface, especially basic groups, which should result in deep dyeing.
Figure 7 shows the relationship between atomic ratios, 0/C and N/C, and total K/S. At a glance, the data are fitted well to two lines. However, both the lines are parallel to the abscissa, which denies the dependence of 0/C or N/C. In the first place, however, the lines are not distinguishing the data sets of 0/C and N/C. The two lines were identified by the pressure at plasma treatment: silk fabrics treated at 60 and 400 Pa shows different dyeability although the atomic ratios are in the same range. It may be a coincidence, but it is interesting that the both 0/C and N/C fitted to a same line

for a same pressure. From the results above, color deepness was found to be more sensitive to plasma condition rather than simple surface chemical composition. An effect of etching caused at lower pressure may be important.

Figure 6. Total K/S of plasma-treated silk fabrics in various plasma conditions after dyed in 10% dye concentration.

Figure 7. Relationship between atomic ratios, 0/C and
N/C, and total K/S. Dye concentration, 10%; plasma condition, 30 min; •, untreated.

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Also in our preliminary study, we treated silk fabrics with NH3 plasma in order to form amino group positively. We found considerably increased N on the silk fabrics, but total K/S did not increase as we expected. The clarification of the mechanism of dyeing and more precise analysis of functional groups are required.
3.2.3. Effect of Dye Concentration
Figure 8 shows total K/S of plasma-treated silk

fabrics at 60 Pa after dyed in various dye concentrations.

As general trends for all three plasmas, total K/S increases with increasing plasma treatment time and dye concentration. Since the normal dye concentration is 10%, total K/S value of 10% dye concentration with 0-min treatment is regarded as the standard. All plasma-treated silk fabrics samples showed higher total K/S values than untreated ones in the corresponding dyeing conditions.
In 02 plasma treatment, although all samples dyed in 4% did not reach the standard, those dyed in 6% and 8% were better than the standard even 5-min treatment.
In N2 plasma treatment, total K/S of 10-min treated silk fabrics in 8% and 6% was almost the same level as the standard. 30-min treated one had

the best total K/S in all dye concentrations, and that dyed in 4% also topped the standard.
In H2 plasma treatment, most of the samples dyed in 6% and 8% showed better total K/S than the standard.

From those results, plasma treatment is obviously useful in dyeing: greater total K/S can be obtained in the same dye concentration, or the same total K/S can be obtained in less dye concentration, which could lead to great saving of dye. The dye concentration can be reduced to as low as 6%, depending on the plasma condition.
The reduction of dye concentration also contributes to the reduction of load on the

environment. After the dyeing,, solid materials (mainly dye) in the used dye solution are usually separated and burned because pure dye is difficult to be recovered from it. In the series of this waste

treatments, it is obvious that less dye contents consume less energy and produce less waste. 3.2.4. Effect of Weight Loss (etching and surface morphology)
Surface roughness (morphology) is a key factor for the color deepness of dyed fabrics. Appropriate roughness enables the surface to hold more dyes and cause random scattering, which results in deep color appearance. Instead of surface roughness, because we have not measured it quantitatively, we examined the effect of weight loss on total K/S. Figure 9 shows relationship between total K/S and weight loss in the plasmatreatment for all plasma gases treated at 60 Pa after dyed in various dye concentrations. There is a clear dependence between them. Total K/S increases with weight loss, and there is little difference among 6-10% of dye concentration. Only 4% is parted from them at lower total K/S. We cannot state the surface

Figure 8. Total K/S of plasma-treated silk fabrics at 60 Pa after dyed in various dye concentrations.

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morphology accurately, but it was found that more etched silk fabrics in any plasma condition had higher total K/S.

3.3. Color Fastness to Wet Rubbing
Results of color fastness to wet rubbing of plasma-treated silk fabrics at 60 Pa after dyed in various dye concentrations are shown in Figure 10, The results are graded from Levels 1 to 5 by human eye. Following a convention, we express a level between, for example, 2 and 3 as Level 2-3. Leve] 5 shows the best performance in color fastness, and Level 2-3 or higher is acceptable for commercial
use.

Other than the judge above, we tried to evaluate the amounts of transferred dye quantitatively, and analyzed the stained cotton fabrics with XPS However, the amount of the dye on the cotton fabrics was so little that XPS could not detect it at all.

Judging by human eye seems to be quite reliable. In the figure, the color fastness of untreated sill fabrics was Level 3-4. The color fastness depend: on not only plasma treatment condition but also dye concentration in dyeing. In general, dyed fabrics with higher K/S (higher color deepness) show lower color fastness. Although higher K/S is achieved b) dyeing in higher dye concentration, color fastness becomes worse. The same thing can be said tc plasma-treated silk fabrics. Most of plasma-treatec silk fabrics had better K/S but it was difficult foi

them to hold the color fastness at higher levels. In addition to the simple discussion with tota] KS, we should consider the effect of surface morphology onthecolorfastness. Surface roughness may be one of the factors for higher K/S, but it car cause higher friction during the rubbing in the test

for the color fastness. Therefore we measured the

friction coefficient of the plasma-treated silk fabrics. Results are shown in Table 1. Thefriction coefficient of untreated silk fabrics is 0.216, while those of 02, N~, and H2 plasma-treated silk fabrics are around 0.7-0.8. It was naturally expected from the SEM photographs (Fig.5), the roughest 02 plasma-treated silk fabrics had the highest coefficient. The higher friction coefficient will easier to damage the fabrics surface in rubbing and will hurt the color fastness. It is easy for the plasma treatment to improve color deepness, but too much treatment spoils color

Figure 9. Relationship between total K/S and weight loss in the plasma treatment for all plasma gases treated at 60 Pa after dyed in various dye concentrations.

Figure 10. Results of color fastness to wet rubbing of
dyed plasma-treated silk fabrics in various dye concentrations. Plasma condition, 60 Pa.

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